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## ERRATA.

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Page.	Line.	
1263	5*	for "Citraconic acid" read "Itaconic acid."
1269	22*	for "Special" read "Spatial."

## VOL. LXXXVI (ABSTR., 1904).

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1032	9*	for "SANDURIN" read "GANDURIN."
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## VOL. C (ABSTR., 1911).

i, 257	15	for "increasing" read "decreasing."
ii, 548	$\left\{ \begin{array}{c} 15^* \\ 14^* \end{array} \right\}$	for " $\frac{c}{s}$ " read " $\frac{c}{os}$ "

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\* From bottom.





CXLIII.—*The Alleged Complexity of Tellurium.*

By AUGUSTUS GEORGE VERNON HARCOURT and  
HERBERT BRERETON BAKER.

THE anomalous position of tellurium in the periodic system has led to many attempts in recent years to separate it into elements of higher and lower atomic weights. Marckwald (*Ber.*, 1897, **40**, 4730), by a laborious process of fractional crystallisation of telluric acid, believed that he had obtained tellurium of atomic weight lower than that of iodine, but on repeating the atomic-weight determinations by a more trustworthy process he arrived at the conclusion that no separation had been effected (Marckwald and Foizik, *Ber.*, 1910, **43**, 1710). Baker and Bennett (*Trans.*, 1897, **91**, 1849) described attempts at separation made by seven distinct methods, none of which afforded any evidence that the element was anything but simple. This conclusion was upheld by the work of Lenher (*J. Amer. Chem. Soc.*, 1899, **31**, 1).

More recently, however, Browning and Flint (*Amer. J. Sci.*, 1909, [iv], **28**, 347) asserted that if tellurium tetrachloride, dissolved in hydrochloric acid, is precipitated by a large excess of hot water, some separation of the element is effected. The work was continued by Flint (*Amer. J. Sci.*, 1910, [iv], **30**, 209). A large quantity of tellurium was purified by precipitation with sulphur dioxide, fusion of the precipitate with potassium cyanide, decomposition of the potassium telluride by air, and distillation of the product in a current of hydrogen. About 1000 grams of this material were converted into the dioxide, and dissolved in the minimum quantity of hydrochloric acid. This was poured into a large excess of boiling water, and allowed to remain. The dioxide which separated was again dissolved in hydrochloric acid, and precipitated by hot water. When this process had been repeated four times, atomic-weight determinations were made with the material, and gave a mean result of 126.59, and after ten repetitions of the same process the atomic weight obtained was only 124.32. No atomic-weight determinations are given in the paper of the less hydrolysable material.

Since this method of fractionation had been used by Baker and Bennett (*loc. cit.*) without success, and since the purification used by Flint was not unexceptionable, it was thought worth while to repeat the work. By the great kindness of Professor Marckwald, 200 grams of telluric acid, which had been recrystallised many times, were placed at our disposal for the purpose. It was not

thought necessary to purify the material further. The acid was boiled with hydrochloric acid until no further odour of chlorine could be observed. The solution of tellurium tetrachloride was evaporated, and dissolved in as small a quantity of hydrochloric acid as possible, the volume of the solution being 150 c.c. This was poured by degrees into 3650 c.c. of water, which was heated to the boiling point, the proportion of tellurium tetrachloride to water being the same as that employed by Flint. The precipitated oxide was dissolved in the minimum quantity of hydrochloric acid, and again partly precipitated by boiling water. The process was repeated until four fractionations had been performed. According to Flint, the dioxide last precipitated should contain tellurium with an atomic weight of nearly a whole unit lower than the accepted atomic weight.

In determining the atomic weight, a method was employed which had given very constant results in the hands of one of us, namely, the conversion of the element into the tetrabromide. To obtain the element, the dioxide was dissolved in hydrochloric acid, and the solution, after heating to the boiling point, was saturated with sulphur dioxide obtained from the liquefied gas. After remaining for a night, the precipitation was complete. The precipitate was washed with boiled distilled water until the washings gave no opalescence with barium chloride. After drying, the tellurium was melted in a current of hydrogen prepared by the electrolysis of purified barium hydroxide solution. The element prepared by this method was obtained in the form of an elongated button showing foliated crystallisation on the upper surface.

The method of determination of the atomic weight was precisely the same as that described in the previous paper. New platinum-plated weights were used, which were carefully standardised. The balance was an Oertling No. 5, which is only used for atomic-weight work. All the weights are calculated to vacuum standard.

The results of the determinations were:

	Weight of tellurium.	TeBr <sub>4</sub> formed.	Atomic weight.
1	0.87822	2.20103	127.55
2	0.69706	1.49640	127.55
3	0.69189	1.73442	127.53
4	0.62732	1.57264	127.53
5	0.58307	1.46162	127.53
		Mean	127.54

Determinations of the atomic weight of the material similarly purified, but without the attempted fractionation, gave a mean result of 127.53. Since no diminution was found in the atomic weight after four partial precipitations, a treatment which Flint had found to result in a diminution of nearly a whole unit in the

atomic weight, we considered it unnecessary to proceed further. It seems possible that the methods of purification used by Flint were insufficient to remove some element of lower equivalent than tellurium, and that this impurity accumulated when the process of fractionation was repeated.

In working up the residues for return to Professor Marckwald, two more precipitations of the tetrachloride by water were effected. In the last precipitation there was noticed a part of the precipitate which was orange in colour. On separation of this from the mass of white dioxide, it was proved to be tellurium trioxide, both by its giving off oxygen when heated alone, and by the evolution of chlorine on treatment with hydrochloric acid.

In order to see if this formation of trioxide afforded any help towards the explanation of Flint's results, some purified tellurium trioxide was treated with nitric acid, and the solution crystallised. The crystals were dried at  $140^{\circ}$ , and on decomposition gave a percentage loss of 17.35, the calculated loss for  $2\text{TeO}_2 \cdot \text{HNO}_3$  being 16.49 ( $\text{Te}=127.54$ ). It thus appears that some formation of the higher nitrate takes place, and it is just possible that this may be the origin of the low atomic weights found by Flint. The atomic weight of the element, on the assumption that only  $2\text{TeO}_2 \cdot \text{HNO}_3$  was present, deduced from this last experiment, would be 118.31. The formation of the trioxide, noted above, has been traced to the purified hydrochloric acid. It was inadvertently left exposed to the bright light prevalent during the last few weeks, and it was found to be seriously contaminated with chlorine.

We wish to express our thanks to Professor Marckwald for the loan of the highly purified telluric acid, and also to Dr. A. Scott for a supply of purified bromine.

CHRIST CHURCH, OXFORD.

#### CXLIV.—*The Solubility of Carbon Dioxide in Beer.*

By ALEXANDER FINDLAY and BUCCHOK SHEN, B.Sc., A.I.C.

THE importance of carbon dioxide for the sparkling quality and the palatability of beer, renders it somewhat remarkable that the solubility of this gas in beer has been studied so little. We have, indeed, found only two investigations of a quantitative character; and as a result of these, the view is most commonly held that beer

absorbs or dissolves more carbon dioxide than a corresponding solution of alcohol in water.

The most extensive and practically the only exact series of determinations of the carbon dioxide in beer are due to T. Langer and W. Schultze (*Zeitsch. für das ges. Brauwesen*, 1879, 2, 369; 1883, 6, 329). The values for the absorption coefficient of carbon dioxide in beer obtained by these investigators are given in table I, which we take from a paper by Emslander and Freundlich (*Zeitsch. physikal. Chem.*, 1904, 49, 317).

TABLE I.

Temp.	Alcohol content in weight per cent.	Absorption coefficient of CO <sub>2</sub> in			Difference between columns 3 and 4.
		Beer.*	Alcohol solution.	Water.	
0.6°	4.265	1.7625 (M)	1.64	1.7508	123 c.c.
1.0	2.996	1.8270 (A)	1.65	1.7207	177 "
1.1	4.303	1.7787 (M)	1.62	1.7133	159 "
1.4	4.341	1.7393 (M)	1.60	1.6913	189 "
2.6	3.022	1.6829 (A)	1.57	1.6060	113 "
2.7	4.381	1.7321 (M)	1.54	1.5991	182 "
2.8	2.709	1.6848 (A)	1.56	1.5923	125 "

\* The letters M and A in this column refer to two different kinds of beer "Märzenbier" and "Abzugbier."

From these figures it would appear that beer absorbs or dissolves considerably more carbon dioxide than the corresponding water-alcohol solution, and even more than water itself. This increased absorption is attributed by Emslander and Freundlich, who discuss this question at length, to the presence in beer of positive colloids, and to the adsorption by these of carbon dioxide. The increased absorption they compare with the increase in the solubility of carbon dioxide in water in presence of ferric hydroxide (Geffcken, *Zeitsch. physikal. Chem.*, 1904, 49, 257; Findlay and Creighton, *Trans.*, 1910, 97, 536).

The chief colloids present in beer are dextrin and albuminoids (in small amount), and the apparent increase in absorption is therefore attributed to these. Such an increase, however, is entirely opposed to the results obtained by Findlay and Creighton, who showed (*loc. cit.*) that the presence of dextrin not only does not increase the solubility of carbon dioxide in water, but, indeed, considerably diminishes it.

In view of the importance of a knowledge of the solubility of carbon dioxide in beer, and in view also of the apparent contradiction between the results obtained by Langer and Schultze and by Findlay and Creighton, we have thought it necessary to investigate

the matter more fully. We have therefore carried out a series of determinations of the solubility of carbon dioxide in solutions of ethyl alcohol in water, in wort, and in beers of different grades.

#### EXPERIMENTAL.

The method employed was the same as that described by Findlay and Creighton. Pure carbon dioxide, however, was used; it was prepared by the action of hydrochloric acid on pure marble. Its solubility in water at 25° was found to be 0.825.

*Solubility of Carbon Dioxide in Solutions of Alcohol in Water at 25°.*—It is known from the experiments of Müller (*Wied. Ann.*, 1889, **37**, 24) that the addition of alcohol (up to about 28 per cent.) lowers the solubility of carbon dioxide in water; but the actual solubility at 25° has not been determined. In table II therefore we give the results of our determinations at this temperature. The concentration of the solutions was obtained from determinations of the density and by interpolation from curves plotted according to the numbers given in the tables of Landolt-Börnstein-Meyerhoffer.

TABLE II.

Concentration: 2.95 grams of alcohol in 100 c.c.;  $d_{15}^{25}=0.99308$ .

Pressure .....	737	836	929	1073	1213	1338
Solubility .....	0.812	0.813	0.812	0.811	0.813	0.811

Concentration: 3.01 grams of alcohol in 100 c.c.;  $d_{15}^{25}=0.99295$ .

Pressure .....	745	823	937	1083	1226	1357
Solubility .....	0.814	0.812	0.815	0.813	0.812	0.812

Concentration: 8.33 grams of alcohol in 100 c.c.;  $d_{15}^{25}=0.98342$ .

Pressure .....	747	846	942	1090	1231	1360
Solubility .....	0.786	0.786	0.784	0.785	0.786	0.788

*Solubility of Carbon Dioxide in Wort.*—The wort employed contained about 13 grams of solids in 100 c.c. In view of the changes which take place on keeping, the determinations of the solubility were carried out with the wort as soon as received. It was de-aerated by boiling under a pressure of 15 mm. of mercury. Table III gives the results of the determinations.

TABLE III.

Pressure .....	745	845	942	1092	1228	1360
Solubility .....	0.743	0.745	0.742	0.742	0.742	0.741
Pressure .....	755	856	955	1106	1250	1375
Solubility .....	0.741	0.743	0.742	0.739	0.738	0.738

*Solubility of Carbon Dioxide in Beer.*—The solubility was determined in three different grades of beer, the general composition of which is shown in table IV. The beer C was a strong beer.

TABLE IV.

	Grams per 100 c.c.		
	<i>A.</i>	<i>B.</i>	<i>C.</i>
Absolute alcohol .....	4.17	5.17	7.13
Maltose and other fermentable carbohydrates..	1.09	1.45	5.57
Malto-dextrin .....	0.20	0.84	0.13
Free dextrin and other unfermentable matter..	2.3	2.92	3.88
Total solids .....	4.32	6.10	11.10

Beer *A* corresponded with the wort employed in the previous determinations.

As the beer contains a certain amount of yeast, there is a continuous, slow formation of carbon dioxide in the liquid. Before determining the solubility, therefore, it was necessary, not only to de-aerate the beer, but also to destroy the yeast. The beer was therefore boiled for some time under a reflux condenser. It was then allowed to cool, and was de-aerated by placing it under a diminished pressure of about 15 mm. for two hours, the temperature being kept below 10° in order to reduce the loss of alcohol to a small amount. The results of the solubility determinations are given in table V. Since "absorption coefficients" are, perhaps, more readily understood than "solubility coefficients," we have also stated our results in that form.

TABLE V.

*Beer A.*

Pressure .....	749	849	944	1090	1227	1353
Solubility .....	0.785	0.785	0.787	0.786	0.786	0.787
Absorption coefficient ...	0.709	0.803	0.896	1.033	1.168	1.284
Pressure .....	752	852	949	1096	1234	1358
Solubility .....	0.786	0.788	0.788	0.789	0.788	0.788
Absorption coefficient ...	0.713	0.809	0.901	1.042	1.172	1.290

*Beer B.*

Pressure .....	750	849	946	1096	1233	1359
Solubility .....	0.759	0.760	0.760	0.760	0.758	0.763
Absorption coefficient ...	0.686	0.778	0.867	1.004	1.127	1.250
Pressure .....	756	858	957	1107	1248	1374
Solubility .....	0.759	0.759	0.761	0.761	0.759	0.761
Absorption coefficient ...	0.692	0.785	0.878	1.015	1.142	1.261

*Beer C.*

Pressure .....	786	871	972	1127	1264	1394
Solubility .....	0.718	0.722	0.723	0.722	0.723	0.725
Absorption coefficient ...	0.663	0.753	0.847	0.981	1.102	1.218
Pressure .....	763	867	968	1123	1260	1389
Solubility .....	0.714	0.717	0.718	0.717	0.719	0.719
Absorption coefficient ...	0.657	0.750	0.838	0.971	1.090	1.204

It may be remarked that absorption of carbon dioxide by beer *C* took place at a comparatively slow rate.

#### Discussion of Results.

From the preceding tables it will be obvious that the solubility of carbon dioxide in wort and in beer is considerably less than the solubility in water. Moreover, if we compare the solubility in beer with that in the corresponding alcohol-water solution, we also find that the solubility is diminished. This is shown in table VI.

TABLE VI.

Per cent. alcohol by weight.	Solubility coefficient of CO <sub>2</sub> in	
	Beer.	Alcohol solution.
4.17	0.787	0.806
5.17	0.759	0.801
7.13	0.718	0.793

That the solubility coefficient in beer diminishes more rapidly than that in the alcohol solution is to be accounted for by the fact that in the beers with the higher alcohol content there is also a larger amount of solid in solution, and these also exercise a lowering effect on the solubility.

The results exhibited in the preceding tables are entirely in harmony with those obtained by Findlay and Creighton (*loc. cit.*; *Biochem. J.*, 1910, 5, 294), who pointed out that surface adsorption is not sufficient in itself to produce a marked increase in the solubility of a gas in water at atmospheric pressure; and that in the few cases in which an increased solubility was observed it seemed most suitable to attribute the effect, except in the case of charcoal and silicic acid, to chemical combination. The possibility of chemical combination in the cases now under discussion appears to be excluded; and the fact that the solubility is independent of the pressure is also in opposition to the assumption of colloidal adsorption (Findlay and Creighton, *loc. cit.*).

How, then, is the discrepancy between our results and those obtained by Langer and Schultze to be explained? An examination of the method of procedure adopted by these investigators points at once to the explanation. The method employed, a modification of that due to Schwackhöfer, was as follows: A flask of about 1 litre capacity was partly exhausted. It was then attached by means of rubber tubing to a tap inserted in the cask of beer to be investigated. The cask was situated in a cool cellar, and the bung-hole was open; 200–300 c.c. of beer were then drawn into the flask, and the barometric pressure and the temperature of the cellar were read at the same time. The amount of carbon



dioxide in the beer was determined by passing the gas evolved through potassium hydroxide.

Although we do not doubt that the amount of carbon dioxide in the beer was accurately determined by this method, we are convinced that the amount so determined does not represent the true solubility of carbon dioxide in beer under the conditions of pressure and temperature prevailing in the cellar; the beer, we believe, *was not merely saturated, but supersaturated*. This belief we shall now attempt to justify.

The phenomenon of gas evolution from solution presents a number of peculiarities, but has not yet been studied to any great extent.\* It is, however, fairly well known, as a matter of everyday experience, that the rate at which a gas is given off from a supersaturated solution (as in the case of soda-water, beer, and other sparkling beverages) is very variable, and depends to a considerable extent on the nature of the liquid. From a few preliminary experiments carried out in this laboratory, it would appear that colloids diminish the rate of evolution of gas, so that the solution may remain supersaturated for a considerable period of time. This behaviour is very marked in the case of beer, and is clearly demonstrated by the following experiments, in which three different kinds of beer, purchased in bottle, were employed, namely, an "Export Beer," an "Extra Stout," and a "Pale Ale."

The bottle of beer was opened carefully without shaking, and was connected immediately either with a manometer or with a gas burette. From the increase of pressure shown by the manometer, or from the volume of gas given off, an indication was given of the rate of evolution of carbon dioxide from the particular beer. The experiments were carried out at room temperature.

(a) *Stout*.—The pressure rose gradually at a rate of about 1.3 mm. of mercury per minute. At the end of about two hours, the bottle was shaken, after which a considerably more rapid evolution of gas was observed: about 3–4 mm. increase of pressure per minute on the average. About twenty-four hours after the commencement of the experiment there still occurred a pressure increase of 126 mm. in ninety-eight minutes; and even after four days the pressure still increased, and the rate of evolution of the gas could be increased by shaking.

In the case of another sample of the same kind of beer, the bottle was connected with a gas burette. Without shaking, the gas was evolved at the rate of about 6 c.c. in the first ten minutes. As the evolution progressed, the rate diminished.

(b) *Export Beer*.—With this beer the rate of evolution of carbon

\* The subject is under investigation in this laboratory.

dioxide was much slower. In about one hundred and fifty minutes the pressure increased to only 79 mm., and the volume of gas given off in the same time was only about 8 c.c. The beer also appeared to be supersaturated to a less extent than the stout.

(c) *Pale Ale*.—In this case the evolution of gas was greater than in either of the previous cases. In ten minutes about 14 c.c. of gas were evolved.

Although we do not claim any great accuracy for these experiments, they seem to show conclusively that considerable time is required for the equilibrium pressure to be established when no shaking occurs.

In the preparation of beer, whether during the primary fermentation or during the after-fermentation in the cask, carbon dioxide is formed in the body of the liquid. It has, however, been shown conclusively by Lamplough (*Proc. Camb. Phil. Soc.*, 1908, **14**, 580), in the case of the decomposition of diazo-salts in solution, that the liquid always becomes supersaturated with gas unless it is subjected to fairly vigorous shaking or stirring. We are therefore justified in assuming that during the fermentation in cask, where there is an absence of mechanical disturbance, the beer becomes supersaturated with carbon dioxide, the rate of escape of gas from solution being less than the rate of its formation. In the case of beer, also, it will probably be found that the evolution is retarded by the presence of colloids and other substances, so that supersaturation is facilitated. In the case of the experiments of Langer and Schultze, therefore, the barometric pressure cannot represent the saturation pressure of the carbon dioxide in the beer; and the amount of carbon dioxide which they found cannot represent the solubility of that gas in beer.

Since the temperature of the beer investigated by Langer and Schultze was only a few degrees above zero, it might be objected that at the much higher temperature employed by us the relationships might be reversed. We have, however, determined the solubility of carbon dioxide in water and in beer also at 12°, but do not find that this objection is a valid one. The solubility of carbon dioxide in water at 12° is 1.158; while the solubility in a beer containing about 4.6 per cent. of alcohol, and about 5 per cent. of solid matter, was 1.080.

If, then, we are right in the interpretation given above of the results obtained by Langer and Schultze, the explanation put forward by Emslander and Freundlich of the alleged increase of solubility of carbon dioxide in beer as compared with its solubility in a corresponding solution of alcohol in water is quite unnecessary, because no such increase is found. We are, however, not at all

unwilling to believe that the colloids present in beer play a very important part in the practical manufacture of a palatable beverage by facilitating the production to a greater or less extent of supersaturation, and, possibly, increasing the persistency of the "head." As previously indicated, however, the question is one which requires to be more fully investigated.

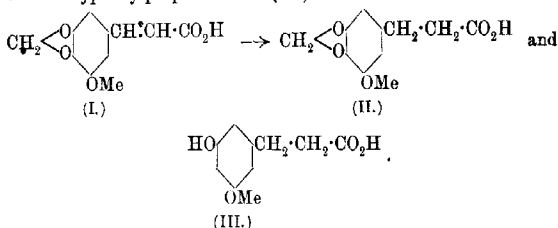
We are indebted to Professor A. J. Brown, F.R.S., for interest taken in this work.

UNIVERSITY OF BIRMINGHAM.

CXLV.—*Synthesis of 4:6-Dimethoxy-2-β-methyl-aminoethylbenzaldehyde.*

By ARTHUR HENRY SALWAY.

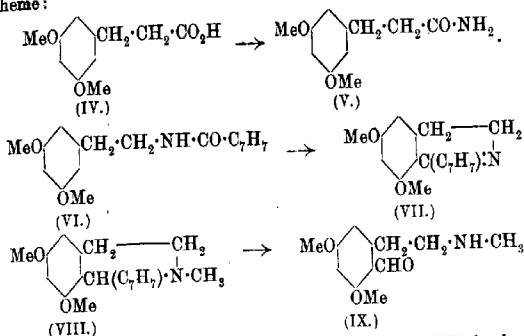
IN a previous communication (Trans., 1910, **97**, 2413) it was shown that 3-methoxy-4:5-methylenedioxyphenylpropionic acid (I) is converted by the action of sodium amalgam into a mixture of β-3-methoxy-4:5-methylenedioxyphenylpropionic acid (II) and β-5-hydroxy-3-methoxyphenylpropionic acid (III):



This reduction was originally conducted with the object of preparing β-3-methoxy-4:5-methylenedioxyphenylpropionic acid (II), from which the synthesis of cotarnine was accomplished by a series of reactions already described (Trans., 1910, **97**, 1208). It now seemed desirable to subject the second reduction product, β-5-hydroxy-3-methoxyphenylpropionic acid (III), to a similar series of allied actions, since the final product thus obtained would be closely allied to cotarnine, and therefore likely to possess valuable therapeutic properties. Accordingly, β-5-hydroxy-3-methoxyphenylpropionic acid (III) was first methylated, and the resulting β-3:5-dimethoxyphenylpropionic acid (IV) transformed successively into

4:6-DIMETHOXY-2- $\beta$ -METHYLAMINOETHYLBENZALDEHYDE. 1321

$\beta$ -3:5-dimethoxyphenylpropionamide (V), phenylacetyl- $\beta$ -3:5-dimethoxyphenylethylamide (VI), 6:8-dimethoxy-1-benzyl-3:4-dihydroisoquinoline (VII), 6:8-dimethoxy-1-benzyl-2-methyl-1:2:3:4-tetrahydroisoquinoline (VIII), and, finally, 4:6-dimethoxy-2- $\beta$ -methylaminoethylbenzaldehyde (IX), according to the following scheme:



4:6-Dimethoxy-2- $\beta$ -methylaminoethylbenzaldehyde (IX) is closely allied to cotarnine and hydrastinine, and is also isomeric with 4:5-dimethoxy-2- $\beta$ -methylaminoethylbenzaldehyde, recently obtained by Pyman (Trans., 1909, 95, 1266) by the oxidation of the alkaloid laudanosine. In view of the fact that each of these compounds possesses valuable therapeutic properties, a physiological examination of the synthetic 4:6-dimethoxy-2- $\beta$ -methylaminoethylbenzaldehyde was desirable, and this has kindly been undertaken by Dr. P. P. Laidlaw, of the Wellcome Physiological Research Laboratories, to whom the author here wishes to express his best thanks. As a result of these experiments it has been shown that whilst the action of the substance on the isolated uterus closely resembles that of cotarnine and 4:5-dimethoxy-2- $\beta$ -methylaminoethylbenzaldehyde, it is considerably less toxic than either of these compounds. When injected into the blood-stream of a cat it produces a rise in blood pressure, accompanied by a slowing of the heart-beat, in this respect having a closer resemblance to 4:5-dimethoxy-2- $\beta$ -methylaminoethylbenzaldehyde than to cotarnine.

#### EXPERIMENTAL.

$\beta$ -3:5-Dimethoxyphenylpropionamide (V, above).

This compound was prepared from  $\beta$ -3:5-dimethoxyphenylpropionic acid (Trans., 1910, 97, 2417) by the successive action of phosphorus pentachloride and ammonia, the method employed being

the same as that already described in connexion with the preparation of  $\beta$ -3-methoxy-4:5-methylenedioxyphenylpropionamide (Trans., 1910, **97**, 1211). The crude acid amide was extracted with chloroform, and the chloroform solution washed with water, dried, and the solvent removed. The oily product thus obtained in almost quantitative yield soon solidified, and was purified by recrystallisation from benzene and petroleum:

0.0978 gave 0.2256  $\text{CO}_2$  and 0.0632  $\text{H}_2\text{O}$ .  $\text{C}=62.9$ ;  $\text{H}=7.2$ .

$\text{C}_{11}\text{H}_{15}\text{O}_3\text{N}$  requires  $\text{C}=63.2$ ;  $\text{H}=7.2$  per cent.

$\beta$ -3 : 5-Dimethoxyphenylpropionamide is readily soluble in benzene, chloroform, or alcohol, but insoluble in light petroleum. It crystallises from a mixture of benzene and petroleum in colourless needles, melting at  $80-81^\circ$ . The fused substance, after resolidification, melts at  $86^\circ$ .

*Phenylacetyl- $\beta$ -3:5-dimethoxyphenylethylamide (VI, p. 1321).*

The above-described acid amide was finely powdered, and shaken continuously with a slight excess of sodium hypochlorite (compare Trans., 1910, **97**, 1212) until the whole had passed into solution. The liquid was then heated to  $100^\circ$  for a short time, and, after cooling, thoroughly extracted with ether. The ethereal solution, which contained the  $\beta$ -3:5-dimethoxyphenylethylamine formed in the reaction, was agitated with small portions of dilute hydrochloric acid until no further quantity of base was extracted. The acid extracts were then united, and shaken with an excess of phenylacetyl chloride in the presence of alkali. The crude phenylacetyl derivative thus obtained did not solidify; it was therefore extracted with ether, the ethereal solution washed successively with dilute hydrochloric acid and water, then dried, and the solvent removed. The residue soon solidified, and was purified by crystallisation from dilute alcohol:

0.1104 gave 0.2918  $\text{CO}_2$  and 0.0701  $\text{H}_2\text{O}$ .  $\text{C}=72.1$ ;  $\text{H}=7.1$ .

$\text{C}_{18}\text{H}_{21}\text{O}_3\text{N}$  requires  $\text{C}=72.2$ ;  $\text{H}=7.0$  per cent.

*Phenylacetyl- $\beta$ -3:5-dimethoxyphenylethylamide* crystallises from dilute alcohol in colourless, prismatic needles, melting at  $73^\circ$ . It is readily soluble in the usual organic solvents, except light petroleum.

In one experiment for the preparation of the above compound a considerable excess of sodium hypochlorite was used, which caused the reaction to take an abnormal course, as indicated by the formation of a phenylacetyl derivative, melting at  $106^\circ$ , instead of  $73^\circ$ . This product was found to contain chlorine, and gave, on analysis, the following result:

4:6-DIMETHOXY-2- $\beta$ -METHYLAMINOETHYLBENZALDEHYDE. 1323

0.1050 gave 0.2498  $\text{CO}_2$  and 0.0575  $\text{H}_2\text{O}$ . C=64.8; H=6.1.

0.2331 „ 0.0990 AgCl. Cl=10.5.

$\text{C}_{18}\text{H}_{20}\text{O}_2\text{NCl}$  requires C=64.8; H=6.0; Cl=10.6 per cent.

The chlorinated base corresponding with this phenylacetyl compound yielded a hydrochloride, which crystallised in radiating clusters of colourless needles, melting at 188°:

0.1096 gave 0.1930  $\text{CO}_2$  and 0.0618  $\text{H}_2\text{O}$ . C=48.0; H=6.3.

0.1510 „ 0.0858 AgCl. Cl (as hydrochloride)=14.1.

$\text{C}_{10}\text{H}_{14}\text{O}_2\text{NCl} \cdot \text{HCl}$  requires C=47.6; H=6.0;

Cl (as hydrochloride)=14.1 per cent.

It is thus evident that in the above experiment one atom of hydrogen had been substituted for one atom of chlorine, and since the chlorinated compound yielded, on oxidation, a monochloro-dimethoxybenzoic acid (m. p. 181—182°) of the formula  $\text{C}_6\text{H}_3\text{O}_4\text{Cl}$  (neutralisation value: Found: 254.6. Calc., 259.1), it follows that the chlorine must be present in the nucleus. The above compound, melting at 188°, is therefore the hydrochloride of  $\beta$ -2(4)-chloro-3:5-dimethoxyphenylethylamine.

6:8-Dimethoxy-1-benzyl-3:4-dihydroisoquinoline (VII, p. 1321).

A quantity (10 grams) of phenylacetyl- $\beta$ -3:5-dimethoxyphenylethylamide was dissolved in xylene, the solution heated to boiling, and phosphoric oxide added in small quantities, with agitation, until a small portion of the xylene solution gave no precipitate of unchanged substance with light petroleum. The solvent was then decanted from the yellow mass of phosphorus compound, and the latter decomposed by warming with an excess of dilute hydrochloric acid. The acid liquid was filtered to remove a little resinous matter, then rendered alkaline, and extracted with ether. After washing with water, the ethereal solution was shaken with small portions of dilute hydrochloric acid until no further basic matter was removed. The extracts were then united, and concentrated to a small volume, when an almost colourless, crystalline hydrochloride was deposited, which was collected and purified by recrystallisation from a mixture of alcohol and ethyl acetate. The yield of pure substance amounted to 8 grams:

1.6464 lost, at 110°, 0.1678  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O}$ =10.2.

$\text{C}_{18}\text{H}_{20}\text{O}_2\text{NCl} \cdot 2\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}$ =10.2 per cent.

0.1060 \* gave 0.2652  $\text{CO}_2$  and 0.0643  $\text{H}_2\text{O}$ . C=68.2; H=6.7.

0.4730 \* „ 0.2140 AgCl. Cl=11.2.

$\text{C}_{18}\text{H}_{20}\text{O}_2\text{NCl}$  requires C=68.0; H=6.3; Cl=11.2 per cent.

6:8-Dimethoxy-1-benzyl-3:4-dihydroisoquinoline hydrochloride is

\* Anhydrous substance.

only moderately soluble in cold water, but readily so in hot, and crystallises from the latter in almost colourless, rhombohedral prisms, which contain two molecules of water of crystallisation, and melt and decompose at  $181^{\circ}$ . It is best crystallised from a mixture of alcohol and ethyl acetate, when it is obtained in stout, colourless prisms. The free base, 6:8-dimethoxy-1-benzyl-3:4-dihydroisoquinoline, when prepared from the pure hydrochloride by addition of alkali, was obtained as a viscid oil, which did not solidify at the ordinary temperature. It yields a *picrate*, which is only moderately soluble in hot water, but readily so in alcohol, from which it crystallises in small, yellow prisms, melting at  $184^{\circ}$ .

6:8-Dimethoxy-1-benzyl-2-methyl-1:2:3:4-tetrahydroisoquinoline  
(VIII, p. 1321).

This compound was prepared by the conversion of 6:8-dimethoxy-1-benzyl-3:4-dihydroisoquinoline into its methochloride, and subsequent reduction with tin and hydrochloric acid, the method employed being identical with that previously described in the preparation of benzylhydrocotarnine from 8-methoxy-6:7-methylene-dioxy-1-benzyl-3:4-dihydroisoquinoline (*Trans.*, 1910, **97**, 1215). The crude product of the reaction was a brown oil, which slowly solidified. It was purified by recrystallisation from light petroleum, from which it separated in stout, colourless, prismatic needles:

0.0927 gave 0.2620  $\text{CO}_2$  and 0.0660  $\text{H}_2\text{O}$ .  $\text{C}=77.1$ ;  $\text{H}=7.9$ .

$\text{C}_{19}\text{H}_{23}\text{O}_2\text{N}$  requires  $\text{C}=76.8$ ;  $\text{H}=7.7$  per cent.

6:8-Dimethoxy-1-benzyl-2-methyl-1:2:3:4-tetrahydroisoquinoline is a crystalline, colourless solid, melting at  $52^{\circ}$ , and is readily soluble in organic solvents. It yields a *picrate*, which is only moderately soluble in hot water, but readily so in alcohol, and crystallises from the latter in small, feathery needles, melting and decomposing at  $195^{\circ}$ .

4:6-Dimethoxy-2- $\beta$ -methylaminoethylbenzaldehyde (IX, p. 1321).

Five grams of 6:8-dimethoxy-1-benzyl-2-methyl-1:2:3:4-tetrahydroisoquinoline, dissolved in dilute sulphuric acid (15 per cent.), were oxidised by heating on the water-bath for about an hour with 4 grams of pyrolusite. An excess of sodium carbonate was then added, and the precipitated manganese carbonate removed by filtration. The filtrate contained, in suspension, some benzaldehyde formed during the oxidation, and was therefore extracted with ether, after which it was rendered strongly alkaline with aqueous sodium hydroxide, and the liberated base dissolved in benzene. The benzene extract was washed with a little water, and then shaken

with successive small portions of dilute hydrobromic acid until no further quantity of base was removed by this treatment. The aqueous solution of hydrobromide thus obtained was concentrated to dryness on the water-bath, and the solid residue purified by crystallisation from a mixture of alcohol and ethyl acetate:

0.2516 (air-dried) lost 0.0148  $\text{H}_2\text{O}$  at  $100^\circ$ .  $\text{H}_2\text{O}=5.9$ .

$\text{C}_{12}\text{H}_{16}\text{O}_2\text{NBr}, \text{H}_2\text{O}$  requires  $\text{H}_2\text{O}=5.9$  per cent.

0.1154 \* gave 0.2138  $\text{CO}_2$  and 0.0608  $\text{H}_2\text{O}$ .  $\text{C}=50.5$ ;  $\text{H}=5.9$ .

0.2219 \* „ 0.1444 AgBr.  $\text{Br}=27.7$ .

$\text{C}_{12}\text{H}_{16}\text{O}_2\text{NBr}$  requires  $\text{C}=50.3$ ;  $\text{H}=5.6$ ;  $\text{Br}=28.0$  per cent.

\* 4:6-Dimethoxy-2- $\beta$ -methylaminoethylbenzaldehyde hydrobromide is readily soluble in alcohol or water, giving deep yellow solutions. It crystallises from a mixture of alcohol and ethyl acetate in pale yellow needles, which contain one molecule of water of crystallisation. The hydrated salt, when heated rapidly, melts at  $100^\circ$ , whilst the anhydrous substance melts without decomposition at  $164^\circ$ . The hydrochloride, owing to its hygroscopic nature, is more difficult to crystallise than the hydrobromide. It separates, however, from absolute alcohol and ethyl acetate in almost colourless, well-formed needles, which contain two molecules of water of crystallisation:

0.2437 (air-dried) lost 0.0304  $\text{H}_2\text{O}$  at  $90^\circ$ .  $\text{H}_2\text{O}=12.5$ .

$\text{C}_{12}\text{H}_{16}\text{O}_2\text{NCl}, 2\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}=13.0$  per cent.

The hydrated hydrochloride melts in its water of crystallisation at  $95^\circ$ . The free base, 4:6-dimethoxy-2- $\beta$ -methylaminoethylbenzaldehyde, was obtained only in the form of a gummy solid on the addition of an excess of sodium hydroxide to a concentrated aqueous solution of the hydrobromide. It is freely soluble in water, but is reprecipitated on the addition of a concentrated aqueous solution of sodium hydroxide. It yields a *picrate*, which is readily soluble in hot water, and crystallises from this solvent in glistening, yellow needles, melting at  $155$ — $156^\circ$ . The *aurichloride* crystallises from hot alcohol in golden-yellow leaflets, which melt at  $131$ — $132^\circ$ :

0.0938 gave 0.0339 Au.  $\text{Au}=36.1$ .

$\text{C}_{12}\text{H}_{16}\text{O}_2\text{N}, \text{AuCl}_4$  requires  $\text{Au}=36.1$  per cent.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,  
LONDON, E. C.

\*. Anhydrous substance.



CXLVI.—*Some New Inorganic Salts.*

By THOMAS VIFOND BARKER.

THE author's previous investigation of isomorphous groups of substances (Trans., 1906, **89**, 1120; *Min. Mag.*, 1907, **14**, 235; 1908, **15**, 42) shows that those members which approach each other nearly in molecular volume are capable of forming zone crystals or parallel growths on each other. For example, in the strictly isomorphous series consisting of potassium, rubidium, and caesium sulphate the molecular volumes are respectively 65.3, 73.8, 85.2; the intermediate member, rubidium sulphate, is capable of forming parallel growths on crystals of either of the others, but the potassium and caesium salts always give irregular deposits on each other. The remarkable crystallographic similarity which exists between the tetragonal mineral scheelite,  $\text{CaWO}_4$ , and the periodates of sodium and ammonium, led the author to the preparation of the periodates of potassium, rubidium, and caesium (Trans., 1908, **93**, 15). The molecular volumes of these periodates are much greater than that of scheelite, and, in accordance with the author's theory, all attempts to obtain parallel growths of them on this mineral have proved fruitless. Since the molecular volumes of lithium salts are, as a rule, lower than those of the corresponding sodium compounds, it seems probable that the parallel growth would be observed if lithium periodate could be obtained. The author has therefore prepared the latter salt, but as it proves not to be isomorphous with the preceding series the fundamental condition necessary for the formation of a parallel growth is absent.

The double chromates of rubidium and caesium with the metal magnesium, which have been prepared for the first time, present considerable chemical and crystallographic interest, for it has been found that the isomorphous relationship which exists between the simple chromates and sulphates also holds for the double salts of the formula  $\text{R}_2\text{Mg}[(\text{Cr}_2\text{S})\text{O}_4]_2 \cdot 6\text{H}_2\text{O}$ . The potassium salt is not comparable, as it crystallises with two molecules of water, but the ammonium salt described by Murmann (*Sitzungsber. K. Akad. Wiss. Wien.*, 1857, **27**, 175) and the rubidium and caesium salts at present described, prove to be isomorphous with the well known series of double sulphates.

*Lithium Periodate*,  $\text{LiIO}_4 \cdot \text{H}_2\text{O}$ .—Rammelsberg (*Pogg. Ann.*, 1868, **134**, 389) prepared a basic salt,  $\text{Li}_4\text{I}_2\text{O}_9 \cdot 3\text{H}_2\text{O}$ , and published satisfactory analytical data; in addition, he obtained from acid

solution another salt which he did not analyse, but from the fact of its being isomorphous with the sodium salt he assumed it to have the composition  $\text{LiIO}_4$ . The author has repeated Rammelsberg's work, and occasionally obtained crystals similar to those of Rammelsberg, but on analysis they invariably proved to consist of sodium periodate. If pure lithium carbonate and periodic acid are used, no tetragonal crystals are ever obtained; no matter whether the salt is crystallised from hot or cold solution, it is always hydrated, and, moreover, crystallises in the hexagonal system. The salt was prepared by dissolving slightly less than the theoretical quantity of lithium carbonate in a solution of periodic acid, and allowing to evaporate in a desiccator over sulphuric acid. The crystals which appear are simple hexagonal prisms; they are generally opaque in the centre, but clear at the edges, and are somewhat deliquescent. A measurement on the goniometer gave  $60^\circ$  angles in the prism zone. Viewed in the polarising microscope under crossed nicols, the crystals, which rest on the basal plane, remain dark on rotation, and in convergent light they exhibit a positive uniaxial figure central. The birefringence is medium. No pyramidal forms were ever observed, so that it was impossible to determine the ratio of the crystallographic axes  $c:a$ . Determinations of the iodine by the Carius method and of the water content were made:

0.3235 gave 0.3539 AgI.  $I=59.14$ .

1.3484 (air-dried) lost 0.1159 at  $200^\circ$ .  $\text{H}_2\text{O}=8.60$ .

$\text{LiIO}_4 \cdot \text{H}_2\text{O}$  requires  $I=58.79$ ;  $\text{H}_2\text{O}=8.34$  per cent.

*Rubidium Magnesium Chromate*,  $\text{Rb}_2\text{Mg}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$ .—This has not been described previously. It was prepared by mixing the proper quantities of solutions of rubidium chromate and magnesium chromate, the former itself being obtained by taking the correct quantities of rubidium hydroxide and chromic acid. Beautiful crystals are obtained by slow evaporation in the desiccator.

The analysis of the salt was kindly undertaken by Mr. H. E. Clarke, of Jesus College, and carried out as follows. A weighed amount of the salt was made up to a standard solution, and divided into two equal portions, one half being used for the magnesium determination by the ordinary phosphate method. The other half was used for the determination of the chromium and rubidium. The solution was reduced in acid solution by addition of ammonium bisulphite, the chromium precipitated as hydroxide, ignited, and weighed. The filtrate was evaporated to dryness, the ammonium salts volatilised, the magnesium removed by ammonium carbonate, and the rubidium ultimately determined as sulphate. The water

follows by difference. The results of two complete analyses are given in the following table:

	(1).	(2).	Mean.	Theory.
Rb <sub>2</sub> O .....	35.05	34.94	35.00	34.89
MgO .....	7.62	7.62	7.62	7.54
CrO <sub>3</sub> .....	37.38	37.54	37.46	37.39
H <sub>2</sub> O by difference ...	—	—	19.92	20.18
			100.00	100.00

The percentage for a corresponding potassium salt would be K<sub>2</sub>O=21.29; MgO=9.11; CrO<sub>3</sub>=45.19; and H<sub>2</sub>O=24.41, so that the analytical results speak for a high degree of purity.

In all, six crystals were measured, five of them by Mr. R. C. Spiller and one by the author. The form and habit of the crystals are in all respects similar to those of the caesium salt, a figure of which is given on p. 1329, but in addition to the forms there depicted small faces were sometimes found replacing the edge between the basal plane and the prism, and having the indices {111} and  $\{\bar{1}\bar{1}\bar{1}\}$ .

System: monoclinic. Ratio of the axes:  $a:b:c=0.7558:1:0.4950$ ;  $\beta=104^{\circ}55'$ . Following is a table of the results obtained by measurement of the two-circle goniometer, together with the corresponding values obtained by calculation.

	No.	Mean observed.		Calculated.	
		$\phi$ .	$\rho$ .	$\phi$ .	$\rho$ .
$m-110$ .....	12	$53^{\circ}51\frac{1}{2}'$	—	—	—
$c-001$ .....	15	89 50	$*14^{\circ}55'$	90°0	—
$r-201$ .....	8	269 48	47 44	270 0	$47^{\circ}26\frac{1}{2}'$
$q-011$ .....	18	27 54	$*29\ 20\frac{1}{2}$	28 17	—

Cleavage: moderately good parallel to  $r-\{201\}$ .

*Caesium Magnesium Chromate*, Cs<sub>2</sub>Mg(CrO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O.—The same method of preparation was employed as for the preceding salt, with which it is strictly isomorphous. In view of this it was only thought necessary to determine the water content:

0.8310 lost 0.1305 H<sub>2</sub>O=15.7.

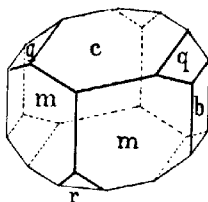
Cs<sub>2</sub>Mg(CrO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O requires H<sub>2</sub>O=16.5 per cent.

Well-defined crystals were obtained by slow evaporation over sulphuric acid; five of them were measured.

System: monoclinic. Ratio of the axes:  $a:b:c=0.7420:1:0.4886$ ;  $\beta=106^{\circ}7'$ . Forms:  $m-\{110\}$ ,  $c-\{001\}$ ,  $b-\{010\}$ ,  $q-\{011\}$ ,  $r-\{201\}$ ,  $o'-\{\bar{1}\bar{1}\bar{1}\}$ , and  $o-\{111\}$ . Out of thirty-five crystals examined with a lens, twenty-two had neither of the latter two forms, eleven had  $\{\bar{1}\bar{1}\bar{1}\}$ , and only four had  $\{111\}$ . A typical crystal is shown in the figure.

Table of Measurements.

	No.	Mean observed.		Calculated.	
		$\phi$ .	$\rho$ .	$\phi$ .	$\rho$ .
b-010 .....	7	0°0'	90°0'	—	—
m-110 .....	28	54 31	90 0	—	—
c-001 .....	5	90 1	16 7	90°0'	—
r-201 .....	9	270 0	47 28	270 0	47°15
q-011 .....	9	30 38	29 35	30 36	—
o-111 .....	2	63 10	47 17	63 22	47°28
o'-111 .....	3	320 46	32 24	320 56	32 11

Cleavage: moderately good, parallel to  $r-\{201\}$ .

The author wishes to express his cordial thanks to Mr. H. E. Clarke for the very full analysis of the rubidium salt, also to Mr. R. C. Spiller, who carried out most of its angular measurements.

MINERALOGICAL DEPARTMENT,  
UNIVERSITY MUSEUM, OXFORD.

### CXLVII.—*The Action of Sodium Hypophosphite on Copper Sulphate in Aqueous Solution.*

By JAMES BRIERLEY FIRTH and JAMES ECKERSLEY MYERS.

THE action of sodium hypophosphite on copper sulphate in aqueous solution has been investigated to some extent by various workers, but there seems to be a diversity of opinion as to the exact nature of the product. It was with the object of arriving at some definite conclusion as to the course of the reaction that the present investigation was undertaken.

Wurtz (*Ann. Chem. Phys.*, 1844, [iii], 11, 250) was of the opinion that in acid solution, or using hypophosphorous acid, the product was pure cuprous hydride ( $\text{Cu}_2\text{H}_2$ ). Berthelot (*Compt. rend.*, 1879, 89, 1005) doubted the existence of such a compound, and accord-

ingly repeated Wurtz's experiments. He obtained a substance which he considered might be regarded as a complex compound of hydroxide and phosphate of copper. In reply, Wurtz (*Compt. rend.*, 1879, **89**, 1066; 1880, **90**, 22) admitted the possibility of the presence of phosphate, but otherwise adhered to his original view. Berthelot's final statement on the matter was that the existence of cuprous hydride was purely hypothetical, since the substance contained constitutional water (*Compt. rend.*, 1879, **89**, 1097).

#### EXPERIMENTAL.

The present investigation is divided into two series of experiments:

- (1) Experiments carried out at the ordinary temperature;
- (2) Experiments carried out at higher temperatures.

*Apparatus*:—The reaction was carried out in all cases in an apparatus in which the precipitation, filtration, and drying are done in an atmosphere of carbon dioxide (Firth and Myers, *Proc.*, 1911, **27**, 96).

##### *Experiments at the Ordinary Temperature.*

A concentrated solution of copper sulphate was prepared from the pure recrystallised salt, and to it was added a moderately concentrated solution of sodium hypophosphite,\* the latter being in slight excess.

A white, flocculent precipitate appeared after a few minutes, which, on addition of a few drops of concentrated sulphuric acid, dissolved, giving a clear blue solution. On keeping, this solution underwent a series of changes. After five or ten minutes, the solution became green, and at the same time a granular, brick-red precipitate settled to the bottom of the tube. The solution was well stirred from time to time, and gradually darkened in colour, the precipitate assuming a reddish-brown, curdy appearance, and increasing in bulk. After about two hours the precipitate was still of the same colour, but a slow evolution of hydrogen commenced, and continued for about an hour. During its production the precipitate darkened, and finally, after the evolution had ceased, was almost black.

On removing the solution and precipitate from the reaction-tube, a film of copper was found on the sides of the vessel. When very thin, it appeared reddish-brown by reflected light and blue by transmitted light.

\* The sodium hypophosphite was freshly prepared, and on treatment with barium nitrate in neutral solution gave only a slight opalescence, indicating that phosphate and phosphite were present only in traces.

From these observations it would appear that the action of sodium hypophosphite in acid solution is not a direct one, but proceeds through a series of stages. It was therefore considered necessary to examine as many of the stages as possible.

*Examination of the Final Precipitate:*—This precipitate was generally collected, after allowing the reaction to proceed over night. It was first thoroughly washed with water saturated with carbon dioxide, then with alcohol, followed by a mixture of alcohol and carbon disulphide. (If the latter is omitted, the precipitate contains free sulphur.) The carbon disulphide was removed by alcohol, and ether was passed through to dry the substance.

The precipitate obtained in this way was placed over calcium chloride in a desiccator, which was then evacuated. No appreciable decomposition of the substance was observed while it was in the desiccator. When thoroughly dry, the precipitate was quite black. Fifteen samples of this precipitate were examined, and it was found that oxygen, phosphate, hydrogen, and copper were invariably present. When quite dry the substance frequently decomposed suddenly on exposure to the air with the evolution of a considerable amount of heat. On one occasion a large desiccator, containing about ten grams of the substance, was shattered owing to the decomposition which was brought about by admitting a little air. Owing to this instability, the analysis of the substance was difficult, and samples were frequently lost when partly analysed.

In all cases the precipitate decomposed suddenly on applying the slightest heat, with the evolution of hydrogen and water-vapour, leaving a violet-coloured residue consisting of metallic copper, phosphate, and oxide. The analysis showed the following proportions:

Cu=83.6; O=7.6;  $P_2O_5$ =6.4 per cent.

When reduced in a stream of dry hydrogen, the residue consisted of metallic copper and phosphate:

Cu=94.8;  $P_2O_5$ =3.8 per cent.

All samples on keeping in moist air became light brown. Such a sample had the following composition:

Cu=78.8; O=18.6;  $P_2O_5$ =1.9 per cent.

On treatment with nitric acid the freshly prepared dry substance produces, first, hydrogen, and afterwards nitrous fumes.

The following table shows the percentage composition of various samples of the substance:

No.	Copper.	Oxygen.	$P_2O_5$ .	Hydrogen.
1.	85.65	6.9	5.2	0.62
2.	82.5	9.73	5.4	0.46
3.	81.3	10.1	6.0	0.62
4.	84.58	8.68	4.7	0.59

*Examination of the Intermediate Precipitates:—*(a) The first precipitate, which was of a brick-red colour, was collected, washed, and dried as before. It was found to contain no hydrogen or phosphate, but only oxygen and copper, and analysis showed that it was almost entirely cuprous oxide. (Found, Cu=89.6; O=10.27. Calc., Cu=88.7; O=11.2 per cent.)

(b) The second stage was taken when the precipitate had darkened in colour and increased in bulk. Samples of this stage gave off hydrogen on heating slightly. The following values were obtained on analysis:

$$\text{Cu}=88.5; \text{O}=10.1; \text{P}_2\text{O}_5=0.74; \text{H}=0.12 \text{ per cent.}$$

*Experiments at Higher Temperatures.*

In this series of experiments the reacting substances were heated to various temperatures from 50° to 90° before mixing. The other details of experiment were the same as with the cold solutions, except that the desiccator in which the substance was kept was not evacuated, but only filled with carbon dioxide.

On mixing the solutions, a dark red precipitate was formed almost immediately, and hydrogen was rapidly evolved. As the precipitate increased in bulk the rate of evolution of the gas also increased. After a short time the precipitate clotted together, and darkened in colour.

On analysis it was found that oxide and phosphate were present in samples which had been prepared at temperatures either higher or lower than from 65° to 70°. It was also noticed that the same constituents appeared in specimens which had occupied more than a few minutes for their preparation.

The following analyses show the percentage composition of precipitates obtained after the reaction had proceeded for two minutes:

(a).	Cu=98.6	H=1.32
(b).	Cu=98.2	H=1.5
(c).	Cu=98.4	H=1.4

Cuprous hydride requires Cu=98.45; H=1.55 per cent.

The following values were obtained from samples occupying longer periods in their preparation. These specimens contained very little hydrogen:

Time.	Copper.	Oxygen.	P <sub>2</sub> O <sub>5</sub> .
45 mins.	91.6	7.0	0.66
70 "	85.7	12.3	1.44

The cuprous hydride prepared in this way is of a reddish-brown colour, and slowly decomposes in moist air at the ordinary temperature. It was therefore found necessary to make the analysis as

soon as the substance was dry. It decomposes suddenly at about  $60^{\circ}$ , with the evolution of hydrogen, leaving a sponge of metallic copper.

*Conclusions.*

In the cold the product of the reaction between an acidified solution of copper sulphate and a solution of sodium hypophosphite is a substance containing copper, hydrogen, phosphorus, and oxygen probably in the form of cuprous oxide, cuprous hydride, and copper phosphate. The instability of this substance is attributed to the co-existence of hydride and oxide. The same solutions at a temperature of about  $70^{\circ}$  interact with the production of cuprous hydride. In order to obtain this compound in a pure state, it is necessary to have the solutions moderately dilute, and to collect the precipitate within a few minutes of the mixing. When dry, the hydride is unstable, and cannot be kept for more than a day.

The difference between carrying out the reaction in the cold and at  $70^{\circ}$  appears to be that in the former case the production of oxide precedes that of hydride, whilst in the latter case the order is reversed.

THE CHEMICAL DEPARTMENT,  
THE UNIVERSITY, MANCHESTER.

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CXLVIII.—*Indicators of the Methyl-red Type.*

By HUBERT HOWARD and FRANK GEO. POPE.

METHYL-RED was first prepared by Rupp and Loose (*Ber.*, 1908, **41**, 3905), and it was suggested by them that it would be useful as an indicator in the titration of weak bases. Their method of preparation was not very satisfactory, and H. T. Tizard (*Trans.*, 1910, **97**, 2485) gave a method of preparation by which almost quantitative yields were obtained. He also determined the strength of methyl-red as an acid and a base, and tested its value as an indicator, showing it to be greatly superior to methyl-orange. In his method of preparation, Tizard states that the alkali salts are very soluble, and that the potassium salt can only be obtained by evaporating an alcoholic solution to dryness, since it is soluble to a considerable extent in ether, and deliquescent in air. We have succeeded, however, in obtaining both the sodium and potassium salts in a crystalline condition, and although specimens of both salts have been kept



for some two or three months, neither as yet shows any signs of deliquescence.

The visible colour change when methyl-red is used as an indicator is from red to yellow, and the indicator can be used for very dilute solutions. We have prepared a number of other compounds of this type, using substituted amines, and find that very sensitive indicators are produced.

#### EXPERIMENTAL.

*Methyl-red*,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , was prepared by Tizard's method, and recrystallised from hot toluene, from which it separates in small prisms, melting at  $183^\circ$ , and closely resembling potassium permanganate in appearance. Apparently, no analysis of methyl-red, other than a nitrogen estimation, has been published; consequently, the following analysis was made:

0.1253 gave 0.3072  $\text{CO}_2$  and 0.063  $\text{H}_2\text{O}$ .  $\text{C}=66.87$ ;  $\text{H}=5.59$ .

0.1274 „ 17.2 c.c.  $\text{N}_2$  (dry) at  $23^\circ$  and 750 mm.  $\text{N}=15.36$ .

$\text{C}_{15}\text{H}_{15}\text{O}_2\text{N}_3$  requires  $\text{C}=66.91$ ;  $\text{H}=5.58$ ;  $\text{N}=15.61$  per cent.

The sodium salt was obtained by grinding 3 grams of methyl-red with 4 c.c. of a 10 per cent. solution of sodium hydroxide (a quantity of alkali, insufficient to convert the whole of the acid into salt). Bright scarlet plates were obtained in this way, and the whole mass was then allowed to remain in a vacuum over sulphuric acid until quite dry. The dry mass was then extracted with boiling toluene, filtered, the residue washed with hot toluene, and finally dried in a vacuum over sulphuric acid:

0.1476 gave 0.0356  $\text{Na}_2\text{SO}_4$ .  $\text{Na}=7.81$ .

$\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_3\text{Na}$  requires  $\text{Na}=7.90$  per cent.

The sodium salt crystallises in scarlet plates, and is readily soluble in water.

The potassium salt was prepared in a similar manner from 3 grams of the acid and 5.6 c.c. of a 10 per cent. solution of potassium hydroxide:

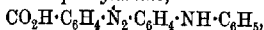
0.0992 gave 0.0234  $\text{K}_2\text{SO}_4$ .  $\text{K}=12.7$ .

$\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_3\text{K}$  requires  $\text{K}=12.7$  per cent.

The salt crystallises in dark red plates, is readily soluble in water, and by working with small quantities may be recovered from this solvent in a crystalline condition.

Attempts were made to prepare the ethyl ester of methyl-red, using Fischer and Speier's method, but the acid was recovered in an unaltered condition from the reaction mixture.

*o*-Carboxybenzeneazodiphenylamine,



was prepared by combining diazotised anthranilic acid with the required amount of diphenylamine dissolved in about thirty times its weight of alcohol. The mixture was allowed to remain for two hours surrounded by ice, and was then heated on a water-bath to 40° for two hours, the precipitate collected, washed, dried, and crystallised from toluene:

0.1168 gave 0.3086 CO<sub>2</sub> and 0.0516 H<sub>2</sub>O. C=72.06; H=4.91.

0.1904 „ 13 c.c. N<sub>2</sub> (dry) at 19° and 736 mm. N=13.45.

C<sub>19</sub>H<sub>15</sub>O<sub>2</sub>N<sub>3</sub> requires C=71.93; H=4.73; N=13.25 per cent.

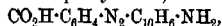
The acid crystallises from toluene in small, olive-green needles, showing a bronze reflex, and melts at 231°.

The sodium salt, as prepared by the method indicated above, crystallises in small, dark red needles, giving an orange-coloured solution in water:

0.1506 gave 0.0322 Na<sub>2</sub>SO<sub>4</sub>. Na=6.93.

C<sub>19</sub>H<sub>14</sub>O<sub>2</sub>N<sub>3</sub>Na requires Na=6.78 per cent.

*o*-Carboxybenzeneazo-*α*-naphthylamine,



was prepared in an analogous manner by combining diazotised anthranilic acid with *α*-naphthylamine in alcoholic solution. The mixture was then allowed to remain for two hours in ice, and finally heated to 40° for two hours. The precipitated azo-compound was collected, washed, and recrystallised from alcohol:

0.1106 gave 0.2844 CO<sub>2</sub> and 0.041 H<sub>2</sub>O. C=70.13; H=4.12.

0.1132 „ 14.3 c.c. N<sub>2</sub> (dry) at 23° and 750 mm. N=14.37.

C<sub>17</sub>H<sub>13</sub>O<sub>2</sub>N<sub>3</sub> requires C=70.10; H=4.46; N=14.43 per cent.

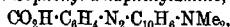
The acid crystallises in minute, green prisms, which exhibit a metallic reflex, and melts at 243°.

The sodium salt crystallises in red needles, and gives a red solution in water:

0.1204 gave 0.0282 Na<sub>2</sub>SO<sub>4</sub>. Na=7.59.

C<sub>17</sub>H<sub>12</sub>O<sub>2</sub>N<sub>3</sub>Na requires Na=7.35 per cent.

*o*-Carboxybenzeneazophenyl-*α*-naphthylamine,



was prepared similarly by combining diazotised anthranilic acid with dimethyl-*α*-naphthylamine in alcoholic solution. The precipitate was collected, washed, dried, and recrystallised from toluene:

0.1274 gave 0.3346 CO<sub>2</sub> and 0.0626 H<sub>2</sub>O. C=71.63; H=5.46.

0.1114 „ 13 c.c. N<sub>2</sub> (dry) at 19° and 736 mm. N=13.21.

C<sub>19</sub>H<sub>17</sub>O<sub>2</sub>N<sub>3</sub> requires C=71.47; H=5.33; N=13.16 per cent.

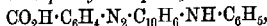
The acid crystallises from toluene in dark green needles, which melt at 196°.

The *sodium* salt is a dark reddish-brown solid, which is somewhat deliquescent:

0.226 gave 0.048  $\text{Na}_2\text{SO}_4$ .  $\text{Na}=6.88$ .

$\text{C}_{19}\text{H}_{16}\text{O}_2\text{N}_3\text{Na}$  requires  $\text{Na}=6.75$  per cent.

*o*-Carboxybenzenesulphonyl- $\alpha$ -naphthylamine,



was prepared in a similar manner, and crystallised from a mixture of alcohol and toluene:

0.1038 gave 0.2854  $\text{CO}_2$  and 0.042  $\text{H}_2\text{O}$ .  $\text{C}=74.99$ ;  $\text{H}=4.5$ .

0.1224 „ 12.43 c.c.  $\text{N}_2$  (dry) at  $19^\circ$  and 736 mm.  $\text{N}=11.80$ .

$\text{C}_{23}\text{H}_{17}\text{O}_2\text{N}_3$  requires  $\text{C}=75.21$ ;  $\text{H}=4.63$ ;  $\text{N}=11.44$  per cent.

The acid crystallises in green needles, which melt at  $238^\circ$ .

The *sodium* salt was obtained by dissolving the acid in hot alcohol, and adding the calculated amount of sodium carbonate dissolved in dilute alcohol. On concentration, the salt separates, and may be recrystallised from water, from which it separates in dark red needles:

0.1696 gave 0.0318  $\text{Na}_2\text{SO}_4$ .  $\text{Na}=6.07$ .

$\text{C}_{23}\text{H}_{16}\text{O}_2\text{N}_3\text{Na}$  requires  $\text{Na}=5.91$  per cent.

The following figures give some data obtained on titrating  $N/100$ -solutions of sodium hydroxide and sodium carbonate with acid, using the preceding azo-compounds as indicators. The indicator was used in the form of a cold saturated solution in alcohol (in which the azo-acid is only very slightly soluble), and two drops were added to 10 c.c. of the alkaline solution in each case. At these dilutions the end-point is quite sharply defined in all cases, much more so than when methyl-orange is used as indicator, and the colour change is more marked. Similar results were obtained in titrating  $N/100$ -solutions of ammonium hydroxide.

	Methyl- orange.	Methyl- red.	$\alpha\text{-C}_{10}\text{H}_7\cdot\text{NH}_2$ derivative.	$\alpha\text{-C}_{10}\text{H}_7\cdot\text{NMe}_2$ derivative.	$\text{NHPh}_2$ deriva- tive.	$\text{C}_{10}\text{H}_7\cdot\text{NHPh}$ deriva- tive.
<i>Volume of N/100-Acid Required.</i>						
$\text{NaOH}$ .....	10.3	10.0	10.0	10.0	10.0	9.95
$\text{Na}_2\text{CO}_3$ ...	10.22	10.0	10.0	10.0	10.0	10.0

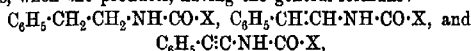
In conclusion, we wish to tender our thanks to the Research Fund Committee of the East London College for a grant which has defrayed the expense of this investigation.

EAST LONDON COLLEGE,  
UNIVERSITY OF LONDON.

CXLIX.—*Dihydrocinnamenyl carbimide* ( $\beta$ -Phenylethyl  
isoCyanate).

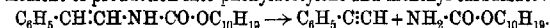
By MARTIN ONSLOW FORSTER and HERMANN STÖTTER.

FROM the point of view of correlating structure and optical activity, it seemed desirable to compare a series of carbamates and carbamides derived from active alcohols and amines by interaction with the azides of dihydrocinnamic, cinnamic, and phenylpropionic acids, when the products, having the general formula:



should illustrate the effect of ethenoid and acetylenoid linkings on specific rotatory power.

It has already been shown that such carbamates and carbamides arise from cinnamenyl carbimide (Trans., 1909, 95, 433), although the action of this compound on menthol had not been studied, and we therefore prepared dihydrocinnamenyl carbimide from dihydrocinnamyl chloride and sodium azide in the expectation that its behaviour would be normal. That is, in fact, the case, and among the derivatives of  $\beta$ -phenylethylamine obtainable therefrom is menthyl dihydrocinnamenyl carbamate; but on attempting to prepare menthyl cinnamenyl carbamate, in order to compare its optical activity with that of the saturated compound, the only recognisable product was found to consist of menthyl carbamate,  $\text{C}_{10}\text{H}_{19}\cdot\text{O}\cdot\text{CO}\cdot\text{NH}_2$ , first described by Arth (*Ann. Chim. Phys.*, 1886, [vi], 7, 464). Since the temperature at which the menthol and cinnamenyl carbimide were heated together was not much higher than that at which the latter had been rectified, it appears probable that the expected menthyl cinnamenyl carbamate breaks up at the moment of production into phenylacetylene and menthyl carbamate:



Although phenylacetylene could not be recognised, probably owing to polymerisation during the continued heating, and although menthyl cinnamenyl carbamate could not be resolved into phenylacetylene and menthyl carbamate, it is nevertheless noteworthy, as bearing on this transformation, that Thiele and Pickard, who first prepared menthyl cinnamenyl carbamate (*Annalen*, 1899, 309, 189), record the production of phenylacetaldehyde by the action of alcoholic potash on that substance, this change involving a disruption between carbon and nitrogen somewhat similar to that just mentioned.

In consequence of this unexpected obstacle and the subsequent

failure to convert phenylpropionyl chloride into the azide, and therefrom generate the isocyanate, the project outlined above has been abandoned.

#### EXPERIMENTAL.

*Dihydrocinnamenylcarbimide (β-Phenylethyl isoCyanate),*  
 $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}:\text{C}:\text{O}.$

The dihydrocinnamyl chloride required for transformation into the azide was prepared by heating 40 grams of dihydrocinnamic acid with 35 grams of thionyl chloride during two hours on the water-bath; this procedure gave a quantitative yield of the chloride, which boiled at 133—135°/21 mm. Preliminary experiments showed that the interaction of the acid chloride and sodium azide is too sluggish at common temperatures to permit of the dihydrocinnamenylazoisimide being isolated, and the higher temperatures at which the change does take place cause nitrogen to be liberated with production of the isocyanate. Fifteen grams of dihydrocinnamyl chloride in 90 c.c. of dry toluene were heated with 7.5 grams of sodium azide during two days on an air-bath under reflux, moisture being excluded from the apparatus. The filtered liquid was then fractionated, and the portion boiling at 112—114°/15 mm. redistilled:

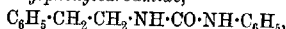
0.2490 gave 21.2 c.c.  $\text{N}_2$  at 18° and 744 mm.  $\text{N} = 9.67.$

$\text{C}_9\text{H}_9\text{ON}$  requires  $\text{N} = 9.52$  per cent.

The isocyanate is a colourless, mobile liquid, boiling at 109—111°/13 mm., and having a faint, slightly pungent odour of cinnamon, whilst the carbimide character of the vapour becomes very pronounced in steam.

#### *Derivatives of Dihydrocinnamenylcarbimide.*

*Dihydrocinnamenylphenylcarbamide,*



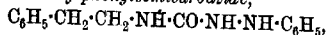
prepared from molecular proportions of the isocyanate and aniline in dry ether, is moderately soluble in boiling alcohol, from which it crystallises in needles, melting to a turbid liquid somewhat indefinitely at 148°:

0.2393 gave 24.8 c.c.  $\text{N}_2$  at 17° and 746 mm.  $\text{N} = 11.74.$

$\text{C}_{15}\text{H}_{16}\text{ON}_2$  requires  $\text{N} = 11.67$  per cent.

The anilide is sparingly soluble in hot benzene, from which it crystallises in lustrous leaflets; it is slightly soluble in boiling petroleum, and dissolves sparingly in boiling chloroform.

*s-Dihydrocinnamenylphenylsemicarbazide,*



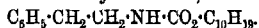
separated immediately on mixing the isocyanate with phenylhydrazine in dry benzene, and crystallises from boiling alcohol in lustrous needles, melting at  $216^{\circ}$ :

0.2145 gave 30.6 c.c.  $N_2$  at  $15^{\circ}$  and 744 mm.  $N=16.27$ .

$C_{15}H_{17}ON_3$  requires  $N=16.47$  per cent.

The substance is moderately soluble in boiling acetone, sparingly so in boiling benzene and chloroform, and insoluble in petroleum.

*Menthyl dihydrocinnamethyl carbamate*,



—Having ascertained that menthol is attacked only very slowly by the isocyanate at the temperature of boiling benzene, 3.5 grams were heated with 3 grams of the carbimide during twenty hours at  $130^{\circ}$ , when the viscous product was submitted to a current of steam. Excess of menthol was quickly removed by this means, and on continuing the process during four days, when nothing further passed over, the residue was found to yield crystals on diluting its solution in alcohol with water. This product was twice recrystallised from dilute acetone, separating in silky needles, which melted at  $86^{\circ}$ :

0.1745 gave 0.4766  $CO_2$  and 0.1503  $H_2O$ .  $C=74.49$ ;  $H=9.63$ .

0.2163 „ 8.7 c.c.  $N_2$  at  $19^{\circ}$  and 761 mm.  $N=4.64$ .

$C_{19}H_{29}O_2N$  requires  $C=75.25$ ;  $H=9.54$ ;  $N=4.62$  per cent.

A solution containing 0.2500 gram, made up to 25 c.c. with absolute alcohol, gave  $\alpha_D -1^{\circ}57'$  in a 3-dm. tube, whence  $[\alpha]_D -65.0^{\circ}$ .

#### *Interaction of Menthol and Cinnamethyl carbimide.*

Cinnamethyl carbimide does not appear to act on menthol when the substances are dissolved in benzene, but on removing the solvent and heating the residue at  $130^{\circ}$  during two days, long, lustrous needles separated when the product cooled. By distillation in steam this material was carried over slowly, and after crystallisation from hot petroleum, melted at  $162-163^{\circ}$ , and gave  $[\alpha]_D -81.6^{\circ}$  in absolute alcohol (0.8 per cent.):

0.1069 gave 0.2601  $CO_2$  and 0.1032  $H_2O$ .  $C=66.35$ ;  $H=10.80$ .

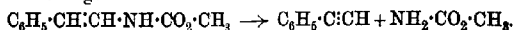
0.2576 „ 16.2 c.c.  $N_2$  at  $21^{\circ}$  and 778 mm.  $N=7.29$ .

$C_{11}H_{21}O_2N$  requires  $C=66.33$ ;  $H=10.55$ ;  $N=7.03$  per cent.

As already explained, this product is not the menthyl cinnamethyl carbamate which might have been expected, but agrees in properties with menthyl carbamate,  $C_{10}H_{19} \cdot O \cdot CO \cdot NH_2$ , formation of which would involve elimination of phenylacetylene. In the hope of being able to recognise the latter, equivalent quantities of menthol and cinnamylazoimide were heated at the melting point

of the last-named until nitrogen ceased to be liberated, when the temperature was raised to  $130^{\circ}$ , and maintained at this point during six to eight hours; although lustrous needles sublimed in the cooler parts of the flask, showing that menthyl carbamate had been produced, phenylacetylene could not be recognised, either in the residue or in the small quantity of viscous material which condensed in the side-tube.

It was thought probable that phenylacetylene might be detected more easily if methyl cinnamenylcarbamate could be subjected to a similar change:



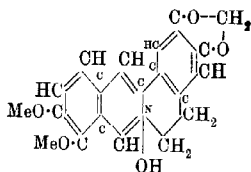
On heating the substance at  $170^{\circ}$  during six hours, however, the greater part of the material was recovered by steam distillation unchanged.

ROYAL COLLEGE OF SCIENCE, LONDON.  
SOUTH KENSINGTON, S.W.

### CL.—*The Constitution of Berberine.*

By CHARLES KENNETH TINKLER.

As the result of a long series of researches on berberine by Perkin (*Trans.*, 1889, 55, 63; 1890, 57, 992; 1910, 97, 321) and others, the constitution of the alkaloid is now represented by the formula (I):

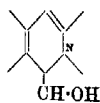


(I.)

It has, however, been pointed out by Gadamer (*Arch. Pharm.*, 1905, 243, 31) that such a substituted ammonium hydroxide would also be capable of representation in the aldehydic (II) or carbinol form (III):



(II.)



(III.)

Perkin and Robinson (Trans., 1910, **97**, 321) state that the salts of berberine must be regarded as derived from the ammonium form of the substance, but the alkaloid itself exists in the corresponding aldehyde modification (II).

Gadamer (*loc. cit.*) has shown that two modifications of berberine can be obtained by the action of alkali hydroxides on the berberine salts. He supposes that berberinium hydroxide (I) is produced in solution by the addition of the calculated quantity of barium hydroxide to a solution of berberine sulphate. The other modification which he supposes is the aldehydic form of the substance (II), and which he has named berberinal, is obtained in the solid state by the addition of excess of sodium hydroxide to the aqueous solution of berberinium hydroxide. The aldehydic form of the alkaloid is the only form of the substance, according to Gadamer, which exists in the solid state. It thus appears that in the case of berberine a difficulty is met with in assigning one or other of the possible formulæ to the substance under various conditions.

In a paper recently published by A. Kaufmann and P. Strübin (*Ber.*, 1911, **44**, 680), purely chemical evidence is adduced in favour of the open-chain or aldehydeamine structure for the pseudobases, which have been investigated by Hantzsch, Decker, and others. In similar cases, however, of carbinol-ammonium base-aldehydeamine isomerism which have been investigated, it has been found impracticable to determine, on purely chemical grounds, which of the various possible formulæ should be assigned to a particular modification of a substance. In several cases important evidence has been obtained from a study of the physico-chemical properties of the substance.

Evidence in favour of the carbinol structure for cotarnine in the solid state and in certain solvents has been obtained from a study of the ultra-violet absorption spectra of the substance and its simple derivatives (Dobbie, Lauder, and Tinkler, Trans., 1903, **83**, 598). The evidence for the production of a carbinol from phenylmethylacridinium iodide by alkalis, originally demonstrated by Hantzsch (*Ber.*, 1899, **32**, 575) by means of conductivity experiments, has been supported by the absorption spectra method of investigation (Dobbie and Tinkler, Trans., 1905, **87**, 269; see, also, Dobbie and Tinkler, Trans., 1904, **85**, 1005; Tinkler, Trans., 1906, **89**, 356).

It may be pointed out that in addition to the physico-chemical evidence for the carbinol structure of these substances, chemical evidence is obtained by a study of the action of potassium cyanide on the substituted cyclic ammonium salts. In this case substances are obtained which are not true salts, but are generally regarded



as derived from the carbinol form of the hydroxide, that is, the cyanogen group of the true cyanide, like the hydroxyl group of the free ammonium base, is mobile.

In the present paper the results obtained by a spectroscopic examination of berberine and its simple derivatives are given. The object of the research was to obtain evidence as to the constitution of the alkaloid under various conditions.

Three derivatives of berberine—berberidic acid, berberine nitrate, and tetrahydroberberine—have previously been examined spectroscopically in showing the relation existing between corydaline and berberine (Dobbie and Lauder, *Trans.*, 1903, **83**, 605). In connexion with the results of that investigation, Hartley (Kayser, *Handbuch der Spectroscopie*, 1905, **3**, 223) states that the second absorption band ( $\lambda=1/3000$ ) shown by dehydrocorydaline and berberine nitrates (1 milligram-molecule in 2500 c.c., 4 mm. to 1 mm.) belongs to the  $\text{NO}_2$  group of the nitrate. This statement, however, has not been verified by the author. Not only do all the berberine salts and the free berberinium hydroxide show this same absorption band at this particular dilution, but nitric acid and nitrates, when examined at such dilutions and in layers of the same thickness as were employed in examining the berberine derivatives, show no absorption bands.

In connexion with the present investigation, the ultra-violet absorption spectra of the following substances have been examined: berberine and its chloride, sulphate, sulphite, and cyanide; methyl-dihydroberberine, berberinal, and the hydro-compound obtained in the decomposition of berberinal.

#### (a) *The Berberine Salts.*

The absorption spectra of berberine chloride, sulphate, and sulphite are almost identical with those of berberine nitrate as determined by Dobbie and Lauder (*loc. cit.*).

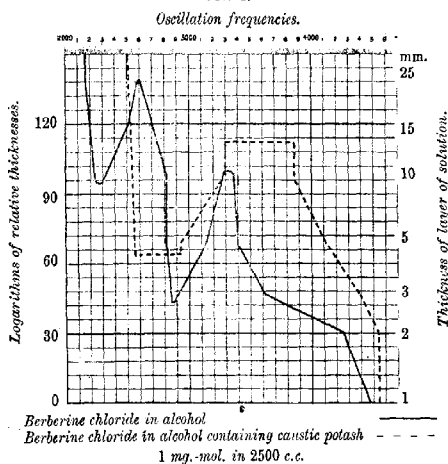
By the addition of a small quantity of an alkali hydroxide to the aqueous solution of the salts, no change in spectra is observed.

It is therefore concluded that berberinium hydroxide and the salts of berberine are constituted in the same manner (I), and that the salts are produced from the alkaloid by the loss of a molecule of water. The absorption curve for the berberine salts is represented in Fig. 1. The curve is drawn according to Baly's method, and so differs from that given by Dobbie and Lauder for berberine nitrate, in having oscillation frequency plotted against logarithms of relative thicknesses instead of actual thickness of layer of solution employed.

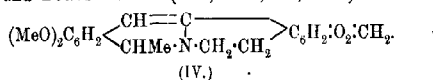
The addition of excess of a soluble base to the aqueous solution

of the salt, or the addition of a small quantity of soluble base to the alcoholic solution of the salt, causes a marked change in the absorption spectra of the solutions. In these spectra only one well-defined absorption band is given, whereas two absorption bands are observed in the spectra of the berberine salts. From the results obtained in other cases, it was expected that the carbinol form of berberine would be produced in these experiments. In order to verify the production of the carbinol, a simple derivative of this form of the alkaloid was sought, in order that its spectra might be compared with those of a solution of a berberine salt

FIG. 1.



containing excess of alkali in the case of the aqueous solution, and a small quantity of alkali in the case of the alcoholic solution. For this purpose methylidihydroberberine (IV) was prepared by Freund and Beck's method (*Ber.*, 1904, **37**, 4677):



There is apparently no doubt as to the constitution of this substance, and in it the linking of the carbon and nitrogen atoms is the same as that in the carbinol form of berberine (formula III).

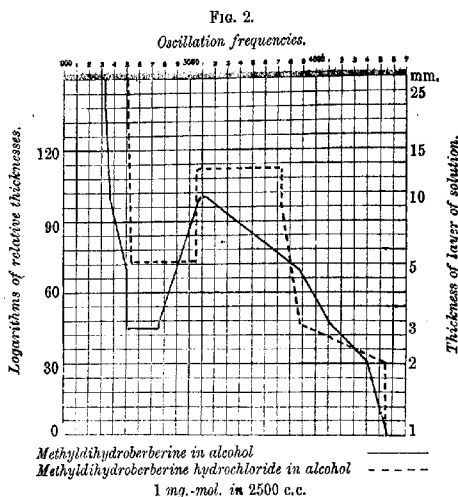
The spectra of methylidihydroberberine and its salts agree closely with those of solutions of the berberine salts containing alkali, and

from this agreement evidence of the formation in these cases of the carbinol form of berberine is obtained.

The spectra of methyldihydroberberine and its salts are shown in Fig. 2, those of berberine chloride in alcohol containing a small quantity of alkali in Fig. 1 (dotted curve).

Evidence of the formation of the carbinol form of berberine in other cases is referred to under the spectra of berberine.

It appeared of interest to examine the spectra of berberine sulphite, as it is stated by Perkin (Trans., 1890, 57, 1098) that



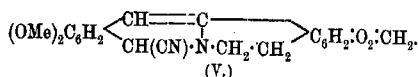
on account of its slight solubility, its constitution was for some time a matter of doubt.

The spectra of berberine sulphite in water and alcohol alone, and in these solvents containing sulphurous acid and sodium sulphite, are identical with each other and with those of the other berberine salts. No indication of the existence of a sulphite derived from the carbinol form of berberine was obtained.

As in the case of cotarnine, phenylmethylacridine, etc., the cyanide of berberine appears to be an abnormal salt, and from the results obtained in previous cases it was expected that berberine cyanide would be a pseudo-cyanide, derived from the carbinol form of the alkaloid (III). The absorption spectra of berberine cyanide in chloroform solution are in close agreement with those of methyl-

dihydroberberine, and are quite different from those of the true berberine salts. An aqueous or alcoholic solution of the cyanide, on the other hand, gives spectra which agree closely with those of the berberine salts. In aqueous solution the substance is probably hydrolysed; in alcohol it may be converted into a true cyanide. By the addition of potassium cyanide to the alcoholic solution of the substance, the spectra of the solution change to those characteristic of the linking in methylidihydroberberine.

The agreement of the spectra of berberine cyanide with those of methylidihydroberberine can only be explained by assigning to the former substance the constitution of cyanodihydroberberine (V):



In addition to the agreement of the spectra of the solutions of methylidihydroberberine, cyanodihydroberberine, and the berberine salts in presence of alkali, these solutions resemble one another in the fact that, unlike the solutions of the berberine salts, they are all fluorescent.

(b) *Berberine.*

The free alkaloid is purified by crystallisation from water. Berberine prepared in this way is insoluble in ether, but chloroform, alcoholic, and aqueous solutions of the substance give spectra which are identical with those of the berberine salts. This agreement of the spectra of the solutions of the alkaloid with those of its salts would point to an ammonium base constitution for the solid substance, if the possibility of tautomeric change were excluded. From the results obtained in other cases, it would be expected that the substance would be stable in chloroform, but would assume the ammonium form in water or alcohol. It would therefore appear from the spectra of the chloroform solution that berberine crystallised from water has the ammonium base constitution in the solid state. Evidence in support of this is afforded by a spectroscopic examination of the other modification of the alkaloid, berberinal, which is soluble in ether (Gadamer, *loc. cit.*).

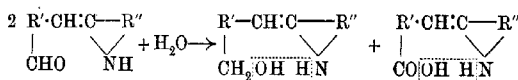
The representation of berberinal as an aldehyde (II) was supported by the formation of an unstable oxime from the substance (Gadamer, *Arch. Pharm.*, 1905, **243**, 31). This substance might, however, be represented as an  $\alpha$ -substituted hydroxylamine, derived from the carbinol form of the base (III), as the evidence obtained from the spectroscopic examination of berberinal points to the fact that the substance is not the aldehydic, but the carbinol, form of

the alkaloid. The spectra of an ethereal\* or chloroform solution of berberinal agree closely with those of methyl-dihydroberberine, and are identical with those of cyanodihydroberberine and an alcoholic solution of a berberine salt containing alkali. This agreement can only be explained by assigning to berberinal the carbinol formula (III), and the name *berberinol* is suggested for this substance.

Since solutions of both the carbinol and ammonium base forms of the substance are obtained by dissolving two different solids in the same solvent, chloroform, these solids must differ in constitution. Berberine crystallised from water is regarded as the ammonium form of the substance (I), and berberinol as the carbinol form (III). No evidence has yet been obtained, by this method of investigation, of the existence of the aldehydic form of the alkaloid (II).

The conversion of berberinol into berberinium hydroxide by means of excess of alcohol, or by solution in water, is readily followed by means of the spectroscope, an aqueous solution of berberinol giving spectra which are identical with those of the berberine salts. The reverse change, the conversion of berberinium hydroxide into berberinol, has been referred to under the berberine salts.

The decomposition of berberinal by the action of a concentrated solution of sodium hydroxide was investigated by Gadamer (*Arch. Pharm.*, 1905, **243**, 31). He supposed that simultaneous oxidation and reduction took place, as in the case of an aromatic aldehyde, with the production of a primary alcohol and an acid, the hydrated forms of dihydroberberine and oxyberberine respectively:

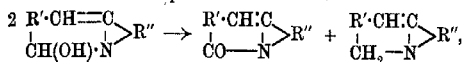


Recently Faltis (*Monatsh.*, 1910, **31**, 565) has suggested that the products of decomposition are oxyberberine and tetrahydroberberine; that is, that the decomposition is similar to that of methylquinoline- $\psi$ -ammonium hydroxide, as suggested by Decker (*Ber.*, 1903, **36**, 2568), three molecules of the substance giving one molecule of the tetrahydro-derivative and two molecules of the oxy-derivative.

The spectra of solutions of the hydro-compound produced in the decomposition of berberinal by excess of sodium hydroxide are identical with those of methyl-dihydroberberine, and quite distinct

\* Since berberinal can be recovered unchanged from ether, the spectra of the ethereal solution are regarded as the spectra of the solid substance.

from those of tetrahydroberberine. The decomposition of the substance can therefore be represented as follows:



two molecules of the carbinol giving one molecule of the oxy-compound and one molecule of the dihydro-compound.

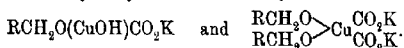
Some of the materials used in this investigation have been purchased by means of a grant from the Research Fund of the Chemical Society, for which the author wishes to express his thanks.

THE UNIVERSITY,  
BIRMINGHAM.

### CLII.—*Cuprighyllates*.

By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.

IN a recent communication (this vol., p. 169) it was shown that those cupri-compounds which are formed by the action of alkalis on copper salts must be regarded as resulting from the addition of CuO to the molecule, and not from the substitution of atoms of copper for hydrogen atoms, either in the alcoholic hydroxyl or in the carboxyl groups. With alcoholic hydroxyl, the addition of CuO may be regarded as a displacement of H by CuOH; in the case of the copper being in the carboxylic portion of the molecule, the presence of (Cu<sup>IV</sup>O)<sup>n</sup> was suggested. The evidence depended on determinations of the minimum molecular weights of six different cupri-compounds of tartaric, saccharic and mucic acids. More positive evidence on this point would, however, be forthcoming if a cupri-salt of a monohydroxy-acid were obtainable, especially if the acid were also monobasic, for the atomic ratio of copper to (say) the potassium present in the potassium salt would then be 1:1, whereas on the theory of the copper displacing the hydrogen of the alcoholic hydroxyl it must be 1:2; thus:



Although such acids yield cupri-salts, it appears to be difficult to obtain them in a definite form: this has been noticed already as regards the quinic acid derivatives (*loc. cit.*, p. 178), and similar difficulties have been found with those of citric, lactic, malic and salicylic acids. Glycollic acid, however, has yielded better results,

and has also supplied another cupri-salt, which is of considerable importance in its bearing on the nature of these compounds.

Copper glycollate may be prepared by double decomposition, or by dissolving copper carbonate in the acid, forming, in either case, small, light blue crystals, which dissolve in water to the extent of 0.1 per cent. Cu at 10°, and 0.46 per cent. at 90°, the solution being quite stable on boiling.

When potassium hydroxide solution (0.04 per cent.) is added to a cold saturated solution of the salt, a light blue, flocculent precipitate of basic copper glycollate begins to form after a certain amount of alkali has been added (about 0.67 KOH for each Cu), and the liquid becomes alkaline when 1.64 K for each Cu has been added: 6.2 per cent. of the total copper remains in solution.

If the potassium hydroxide solution is added to the solid copper glycollate, the same proportion (1.61 KOH) is required to produce alkalinity, but the whole of the copper remains in solution, apparently in a colloidal condition; for the solution is opalescent, and can rarely be filtered. On the one occasion when it was successfully filtered, no trace of precipitate was left on the filter. If rather more water is present when the alkali is added, the whole liquid gelatinises.

When to the barely alkaline liquid obtained as above, excess of alcohol is added, a light blue, flocculent precipitate is formed, which consists of an imperfect emulsion. If this is filtered off rapidly (which is not always possible, owing to the emulsion de-emulsifying, and blocking the filter), it may be dried in a vacuum, and then at 140°. At 100° it is not quite anhydrous; and above 140° it begins to decompose.

It forms a light blue neutral powder, decomposed by water. Analyses of four preparations of it dried at this temperature gave:

	Cu.	K.	Ratio.
	30.59	18.39	1 : 0.98
	30.63	16.63	1 : 0.88
	30.99	18.03	1 : 0.95
	30.14	17.45	1 : 0.94
Mean .....	30.59	17.63	1 : 0.94
Theory for $\text{CH}_2\text{O}(\text{CuOH})\text{CO}_2\text{K}, \text{H}_2\text{O}$	30.03	18.47	1 : 1

Considering that no method of purification is available, these values agree as nearly as can be expected with the formula given, and are conclusive against the ratio of copper to potassium being 1:2, as required on the view that the copper displaces an equivalent of hydrogen. The ratio in every case is rather more than 1:1, the potassium being displaced to a certain extent through

the action of water by some copper, as occurs in the case of all the cupri-compounds hitherto investigated.

The formula, as will be seen, represents a molecule of water as being present, and, since that cannot be eliminated without involving decomposition, the compound is probably an hydrol, containing the group  $C(OH)_2OK$ .

*γ-Cupriglycollates*.—The transformation of an ordinary copper salts containing  $(CO_2)_2Cu$  into a  $\beta$ -cupri-salt containing



has been represented as due, in part, to the tendency of the carbon atom to unite with OH and OK; and it was suggested that in the deep violet-blue liquids produced by the action of excess of alkali, which act on cellulose, this process has been carried a step further, the quadrivalent copper atom having, like the carbon atom, attracted to itself OH and OK, forming a cuprite group. These were termed  $\gamma$ -compounds. Attempts to isolate them in various cases were unsuccessful, but the ultimate product of the action of lime on copper sulphate is a substance showing the same colour and reactions as the  $\gamma$ -cupri-compounds, and, in its case, there must be a cuprite group present, for its formula is  $CuO(CaO)$  (Trans., 1907, 91, 1995; 1910, 97, 1858). In the case of the glycollate, the  $\gamma$ -cupri-salt has now been isolated.

In the preparation of the cupriglycollate already described, the addition of alcohol leaves from 3 to 12 per cent. of the total copper in solution, and after some time this separates in the form of violet crystals (hence the necessity, mentioned above, for filtering off the emulsion as rapidly as possible): these crystals may, however, be obtained in larger quantities by treating the solid glycollate with excess of potassium hydroxide before adding the alcohol: the excess of alkali, unless very considerable, causes a precipitation of basic copper glycollate, leaving about 40 per cent. of the total copper in solution, and the addition of alcohol then precipitates no emulsion, but a gradual separation of the above-mentioned violet crystals takes place. These appear to be of considerable size, but are found to be made up of bundles of soft, hair-like crystals: they are easily washed with alcohol, and, when dried, are of a mauve colour, unlike any ordinary copper salt. With water they give a strongly alkaline reaction, and are decomposed into a basic salt: in ordinary moist air they absorb carbon dioxide. They continue to be deposited from the alcoholic liquid during some forty-eight hours, only traces of copper remaining in solution, and the first and last crops give the same values on analysis. They suffer no change at  $100^\circ$ , but at  $135^\circ$  they lose water, and become lavender-

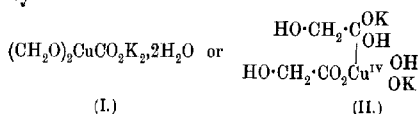


blue, decomposing at a higher temperature. The blue product on exposure to air gradually absorbs water, and becomes mauve again.

The proportions of alkali used were varied from 2 KOH to 10 KOH for each Cu present, the only difference noticeable under such variation being that with the higher proportions the amount of basic glycollate precipitated was considerably reduced, and the crystals were larger and more like tables than needles. Five preparations, of which No. V was obtained with 10 KOH, gave the following values: (No. I was of doubtful purity, and has been excluded from the mean):

	Cu.	K.	H <sub>2</sub> O.	Ratio.
I.	18.26	24.97	10.11	1 : 2.22 : 1.97
II.	18.96	23.61	10.83	1 : 2.02 : 2.02
III.	19.47	22.69	10.56	1 : 1.90 : 1.91
IV.	19.19	23.20	10.79	1 : 1.97 : 1.98
V.	19.09	23.33	( 6.37)	1 : 2.03 : (1.18)
Mean .....	19.20	23.33	10.73	1 : 1.98 : 1.97
Calculated	19.51	24.00	11.06	1 : 2.00 : 2.00

The calculated values may be deduced from compounds represented by:



The former agrees with the amount of water lost on heating in most cases, but must be rejected on account of the substance being strongly alkaline, which property is accounted for by the  $\gamma$ -cupri-glycollate formula, II, although the loss of the elements of  $2\text{H}_2\text{O}$  by such a substance can only be explained by its becoming transformed into the anhydrous form of No. I: a view which admits of the existence of cupri-salts formed by the substitution of copper for the hydrogen in alcoholic hydroxyl groups, although these may not be obtainable by the direct action of an alkali on copper salts. A change of this sort is of a somewhat profound character, but it is in accordance with the dehydration being accompanied by a loss of the characteristic mauve colour. It is also noticeable that in the case of preparation V, where the crystal appeared somewhat different in form, only half this amount of water was lost before decomposition began. A substance represented by formula II could lose  $1\text{H}_2\text{O}$  with little alteration in structure.

The hydroxides of the other alkali metals behave similarly to that of potassium, certain gradational differences being observable throughout the series. The equivalents required to produce alkalinity are: 1.5 M/OH with lithium, 1.64 with sodium and potassium (and also with barium), 1.67 with rubidium, and 1.77

with caesium. In all cases, the barely alkaline liquids are opalescent and unfilterable, excess of alkali producing a precipitate of basic salt, and the liquid becoming filterable. The  $\gamma$ -cupri-salts are thrown down on the addition of alcohol with greater difficulty as the atomic weight increases: the sodium salt is precipitated at once, the potassium salt begins to form in a few minutes, the rubidium salt forms much more slowly, and the yield is a very poor one, whilst the caesium salt is not thrown down at all. The further addition of ether in this case causes the separation of a few drops of deep blue liquid, which apparently contain the  $\gamma$ -compound, but mixed with a large excess of caesium hydroxide.

The rubidium salt is very similar to the potassium compound, but it forms larger crystals, and these are of a somewhat darker mauve colour. On heating, it gives off  $1\text{H}_2\text{O}$  at  $140^\circ$ , like the preparation V of the potassium salt, and decomposes at  $150^\circ$ . On analysis, after drying at  $100^\circ$ , it gave:

	Cu.	Rb.	H <sub>2</sub> O.	Ratio.
	15.01	40.48	4.24	1 : 2.01 : 1.0
Calculated	15.19	40.83	4.31	1 : 2.00 : 1.0

The sodium salt differs from the others in forming much finer, less-defined crystals, and in being violet, instead of mauve, on drying. Its composition, also, does not appear to be so simple as in other cases. Four preparations, obtained under different conditions, gave:

	Cu.	Na.	H <sub>2</sub> O.	Ratio.
	21.61	16.37	(10.72)	1 : 2.09 : (1.73)
	21.38	17.22	7.45	1 : 2.23 : 1.28
	21.51	16.61	7.02	1 : 2.18 : 1.15
	21.75	16.88	7.32	1 : 2.15 : 1.19
Mean .....	21.56	16.77	7.29	1 : 2.16 : 1.19

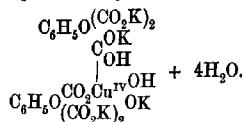
In the case of lithium, no similar compound was obtained, the addition of alcohol causing only a very small precipitation of an amorphous solid.

Barium probably forms a  $\gamma$ -cupriglycollate, but the violet substance obtained was mixed with excess of barium hydroxide precipitated by the alcohol.

No indications of the formation of a calcium compound were obtained.

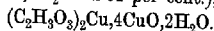
It is not improbable that the alkaline cupricitrate discovered by Luff has the same constitution as that suggested for the  $\gamma$ -cupriglycollates, instead of that previously suggested by the present author (*Trans.*, 1910, **97**, 1844), for one of the conclusions drawn respecting it requires correction. It was found that its alkalinity was equivalent to one-sixth of the potassium present, and it was concluded, therefore, that one of the six potassium atoms was in

the "alkaline" condition. It seems impossible, however, to determine the actual number of atoms which are present in this condition, for, when the compound is decomposed, part of the potassium hydroxide liberated may produce an equivalent of copper oxide, forming a basic salt, or a neutral cupri-salt. The potassium- $\gamma$ -cupriglycollate, for instance, shows an alkalinity, when neutralised by acid, of only 0.3 K, a basic salt being precipitated. Luff's salt may, therefore, easily contain two atoms of "alkaline" potassium, and be represented by:



It presents the same difficulty as the  $\gamma$ -cupriglycollate, in losing  $6\text{H}_2\text{O}$  when heated, as if it were  $(\text{C}_6\text{H}_5\text{O})_2\text{Cu}(\text{CO}_2\text{K})_6 \cdot 6\text{H}_2\text{O}$  (copper displacing hydrogen in hydroxyl), although such a formula is inconsistent with its alkalinity. Luff's salt forms large, violet-blue crystals, unlike those of the potassium and rubidium cupriglycollates, but this difference may be due to the presence of water of crystallisation, for the colour of the crystals is similar to that of the  $\gamma$ -cupriglycollates when in solution, or even when moist.

*Basic Glycollates.*—The proportion of 1.64 KOH to each molecule of copper glycollate in weak solution necessary to produce alkalinity would indicate—if all the copper were precipitated, as was nearly the case—the formation of a basic glycollate approximating  $(\text{C}_2\text{H}_3\text{O}_3)_2\text{Cu} \cdot 5\text{CuO}$ , and such was found to be the composition of the precipitate obtained, with  $5\text{H}_2\text{O}$  retained at  $100^\circ$  and almost eliminated at  $145^\circ$ . (Found, Cu=54.54;  $\text{H}_2\text{O}$ =11.15. Calc., Cu=54.37;  $\text{H}_2\text{O}$ =12.84 per cent.) It is a bulky, fairly dark blue precipitate, which must be dried in a vacuum before being heated at  $100^\circ$ , or it partly decomposes, and also forms carbonate. In some other experiments in which a smaller proportion of alkali was added, and in which less water was present, two other basic salts were repeatedly obtained, one as a light blue, opaque precipitate, the other much darker and more transparent in appearance. Both of these suffered no decomposition on drying at  $100^\circ$ , and both became anhydrous at  $145$ – $160^\circ$ . The former consisted of  $(\text{C}_2\text{H}_3\text{O}_3)_2\text{Cu} \cdot 2\text{CuO} \cdot \text{H}_2\text{O}$  (Found, Cu=48.90;  $\text{H}_2\text{O}$ =4.79. Calc., Cu=48.80;  $\text{H}_2\text{O}$ =4.61 per cent.), the latter of



(Found, Cu=56.78;  $\text{H}_2\text{O}$ =6.25. Calc., Cu=55.97;  $\text{H}_2\text{O}$ =6.35 per cent.)

A cupriglycollate of the formula  $(\text{C}_2\text{H}_3\text{O}_3)_7\text{Cu}_4\text{K}$ , obtained by the

action of copper acetate on potassium glycollate, has been mentioned previously (this vol., p. 810), but its constitution has not been investigated.

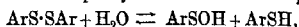
The author takes the present opportunity of expressing his acknowledgment of assistance obtained from the Research Fund of the Chemical Society in his investigation of copper compounds.

HARPENDEN.

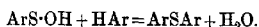
### CLII.—*The Synthesis of Derivatives of Thioxanthone from Aromatic Disulphides.*

By EFFIE GWENDOLINE MARSDEN and SAMUEL SMILES.

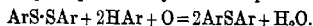
IN a previous paper (Prescott and Smiles, this vol., p. 640) it was shown that aromatic disulphides are decomposed by concentrated sulphuric acid into a sulphonylic acid and a mercaptan:



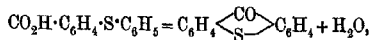
and further reasons were given for supposing that this reaction is reversible, the equilibrium in ordinary cases being greatly in favour of the disulphide. When, however, a suitable aromatic compound is added to the mixture, the sulphonylic acid, being then converted into an unsymmetrical monosulphide, is removed, and the equilibrium is disturbed:



If a sufficient quantity of the aromatic derivative is present, the disulphide may be completely converted into monosulphide. Meanwhile, the mercaptan, which now appears in excess, is oxidised by the sulphuric acid (Stenhouse, *Annalen*, 1861, **149**, 250) to the original disulphide, which becomes available for renewed decomposition. The complete process may thus be represented as follows:



When di-*o*-thiobenzoic acid was condensed with benzene in this manner it was found that thioxanthone was obtained; this substance is evidently formed by elimination of water from the unsymmetrical monosulphide, *o*-phenylthiolbenzoic acid:



which is produced in the first phase of the interaction.

In the present paper it is shown that this method may be applied to the synthesis of more complex derivatives of varied character.

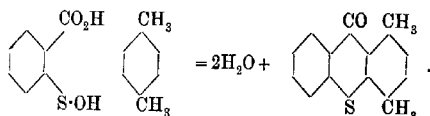
Generally speaking, the methods of synthesising thioxanthenes from disulphides may be said to fall under either of two types:

(1) In one of these the carboxyl group which is to form the carbonyl of the thioxanthone is present in the disulphide chosen, and in this case the starting material may be di-*o*-thiobenzoic acid or its derivatives, which are submitted to condensation with any aromatic compound.

(2) In the second type the carboxyl is present in the aromatic compound chosen for condensation. Here any suitable disulphide may be chosen for condensation with suitably substituted derivatives of benzoic acid; for example, *m*-hydroxybenzoic acid.

It is obvious that either of these methods may be varied to a very great extent; but since no useful end would be served in preparing numerous complex derivatives of thioxanthone, we have limited our experiments to mere illustration.

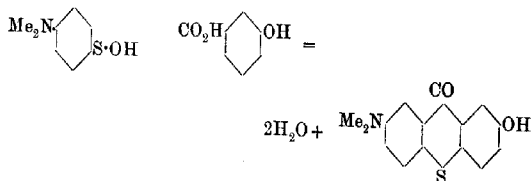
To exemplify the first type of synthesis, di-*o*-thiobenzoic acid has been condensed chiefly with disubstituted derivatives of benzene of varying character: halogen derivatives, phenol, and hydrocarbons. The thioxanthenes which are formed contain one of the aromatic nuclei unsubstituted; for example:



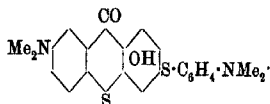
To illustrate the second type of synthesis, *p*-dithiodimethylaniline has been condensed with *m*-hydroxybenzoic acid. It has been shown that on the condensation of this disulphide with phenol, the greater portion of the product consists of complex substances, which are formed by the further action of the sulphylic acid,



on the initial unsymmetrical sulphide. A similar type of reaction has been observed with *m*-hydroxybenzoic acid; for the product is not the simple hydroxydimethylaminothioxanthone which might be expected according to the scheme:

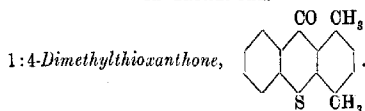


but is the dimethylaminophenylthiol derivative of this:



Two isomeric substances have been isolated from this process; they probably differ in the varying situation of the  $\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$  residue.

#### EXPERIMENTAL.

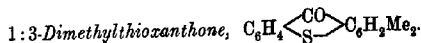


The di-*o*-thiobenzoic acid employed in these experiments was obtained by oxidising *o*-thiolbenzoic acid with ferric chloride (Prescott and Smiles, this vol., p. 644). This acid, in quantities of about 10 grams at a time, was mixed with 50 c.c. of concentrated sulphuric acid and excess of *p*-xylene. Interaction immediately began with evolution of sulphurous acid, but it was hastened to completion by warming the mixture on the water-bath to  $50^\circ$  for three-quarters of an hour. During the process the mixture was constantly shaken. The precipitate, which separated on pouring the mixture into water, was collected, and washed with water; finally, it was treated with aqueous alkali hydroxide to remove any unchanged dithio-acid. The solid residue was again collected, and washed with water until free from alkali hydroxide. Recrystallisation of the dried substance from boiling alcohol furnished 1:4-dimethylthioxanthone in short, yellow needles, which melted at  $112^\circ$ :

0.1910 gave 0.5234  $\text{CO}_2$  and 0.0866  $\text{H}_2\text{O}$ .  $\text{C}=74.7$ ;  $\text{H}=5.0$ .

$\text{C}_{16}\text{H}_{12}\text{OS}$  requires  $\text{C}=75.0$ ;  $\text{H}=5.0$  per cent.

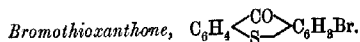
The substance exhibits a bright fluorescence in most organic solvents; the solution in concentrated sulphuric acid shows a yellow fluorescence. In the preparation of this substance it is important to observe that the acid solution should not be heated much above the limit given; otherwise, very insoluble products—probably bithioxanthenes—are formed.



The condensation of di-*o*-thiobenzoic acid was conducted with *m*-xylene, as just described with *p*-xylene. The product crystallised from boiling alcohol in silky, yellow needles, which melted at 127°. The substance exhibits a blue fluorescence in alcoholic solution, and a green in sulphuric acid:

0.1860 gave 0.5100 CO<sub>2</sub> and 0.0870 H<sub>2</sub>O. C=74.7; H=5.2.

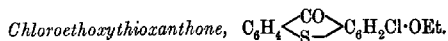
C<sub>15</sub>H<sub>12</sub>OS requires C=75.0; H=5.0 per cent.



The condensation of bromobenzene and di-*o*-thiobenzoic acid was carried out as before. The product was crystallised from alcohol, when it was obtained in minute, yellow needles, which melted at 141°:

0.1930 gave 0.3790 CO<sub>2</sub> and 0.0408 H<sub>2</sub>O. C=53.5; H=2.3.

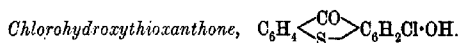
C<sub>13</sub>H<sub>7</sub>OBrs requires C=53.6; H=2.4 per cent.



*p*-Chlorophenetole was condensed with di-*o*-thiobenzoic acid by means of warm sulphuric acid. The product was freed from acid impurities by means of alkali, and then recrystallised from boiling alcohol; *chloroethoxythioxanthone* was thus obtained in slender, yellow needles, which melted at 144°:

0.1986 gave 0.4528 CO<sub>2</sub> and 0.0748 H<sub>2</sub>O. C=62.6; H=4.1.

C<sub>15</sub>H<sub>11</sub>O<sub>2</sub>ClS requires C=62.7; H=3.8 per cent.



A mixture of di-*o*-thiobenzoic acid and excess of *p*-chlorophenol was warmed on the water-bath with concentrated sulphuric acid. When the interaction was complete, the mixture was poured into water, and the solid precipitate was collected and redissolved in aqueous alkali hydroxide. The phenol was liberated from this solution by saturation with carbon dioxide; it was collected and recrystallised from alcohol, in which it is sparingly soluble. Finally, the chlorohydroxythioxanthone was obtained in yellow needles, which melted at 253°:

0.2010 gave 0.1094 AgCl.  $C=13.5$ .

0.1076 „ 0.2362  $CO_2$  and 0.0305  $H_2O$ .  $C=59.8$ ;  $H=3.1$ .

$C_{13}H_7O_2ClS$  requires  $C=59.4$ ;  $H=2.6$ ;  $Cl=13.5$  per cent.

The sodium salt of this phenol forms orange needles, which are sparingly soluble in cold water. The substance exhibits a faint green fluorescence in sulphuric acid, the solution being orange.

#### *Condensation of Di-p-thiodimethylaniline.*

Preliminary experiments on the condensation of this disulphide with *m*-hydroxybenzoic acid showed that in sulphuric acid the second molecular proportion of the dimethylanilinesulphoxylic acid,  $NMe_2 \cdot C_6H_4 \cdot S \cdot OH$ , united with the thioxanthone which was produced by condensation of the first with the *m*-hydroxybenzoic acid (see p. 643). Therefore, in order to obtain maximum yields of the product, the disulphide and *m*-hydroxybenzoic acid were employed in equimolecular proportions. The solution of these substances in concentrated sulphuric acid was heated at  $60-70^\circ$  on the water-bath until evolution of sulphurous acid had ceased. This usually occupied about an hour, and after the lapse of that time the solution had become dark red. The mixture was then poured on crushed ice, and the liquid was rendered alkaline with sodium carbonate. After the mixture had been kept for some hours, the precipitated material solidified; this was collected, and as completely as possible freed from excess of alkali by washing with water. On treating the product with hot alcohol, a considerable portion readily dissolved, whilst the residue was almost insoluble. The latter was recrystallised from boiling phenetole, in which it was sparingly soluble. The dimethylaminophenylthiol derivative of hydroxydimethylaminothioxanthone which was thus obtained formed garnet-coloured prisms. When rapidly heated, the substance melts at  $250^\circ$ ; it is sparingly soluble in most organic media, and the dilute solution in chloroform exhibits a green fluorescence:

0.1075 gave 0.2564  $CO_2$  and 0.0514  $H_2O$ .  $C=65.0$ ;  $H=5.3$ .

0.1515 „ 0.1698  $BaSO_4$ .  $S=15.4$ .

$C_{23}H_{22}O_2N_2S_2$  requires  $C=65.4$ ;  $H=5.2$ ;  $S=15.1$  per cent.

The salts of this base are sparingly soluble, yellow substances; the platinumchloride was obtained by adding chloroplatinic acid to an alcoholic solution of the chloride. It forms an insoluble yellow powder of high melting point. Attempts to purify the substance were not successful on account of its insolubility in common media and instability in solvents of high boiling point. A sample which had been dried at  $100^\circ$  was analysed:—



0.1478 gave 0.0328 Pt. Pt=22.2.

$C_{25}H_{22}O_2N_2S_2H_2PtCl_6$  requires Pt=22.9 per cent.

The scarlet sodium salt of this thioxanthone derivative is insoluble in cold water, and is decomposed by carbonic acid.

That portion of the original product which was soluble in hot alcohol was reprecipitated by the addition of water and a little glacial acetic acid. This process was repeated several times until a substance of constant composition was obtained. The product formed a bright orange powder of similar properties to the thioxanthone derivative previously described. It is more soluble in organic media than that substance, and exhibits a brighter fluorescence in chloroform solution; the sodium salt and hydrochloride also are more soluble in water. Analysis showed that the substance is undoubtedly an isomeride containing an additional molecular proportion of water. The data quoted were obtained with samples from different preparations dried in a vacuum desiccator:

0.1074 gave 0.2456  $CO_2$  and 0.0350  $H_2O$ . C=62.36; H=5.7.

0.1123 „ 0.2563  $CO_2$  „ 0.0580  $H_2O$ . C=62.2; H=5.2.

0.1650 „ 8.2 c.c.  $N_2$  (moist) at 14° and 76 mm. N=5.9.

$C_{25}H_{22}O_2N_2S_2H_2O$  requires C=62.7; H=5.4; N=6.3 per cent.

When heated in the steam-oven the substance contracts with partial loss of water, but this could not be estimated for; even at 150° it is not completely expelled, and the substance then begins to decompose.

The yield of these two derivatives of thioxanthone was almost theoretical.

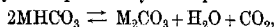
In conclusion, we desire to thank the Research Fund Committee of the Society for a grant which has defrayed the expenses of these experiments.

THE ORGANIC CHEMISTRY LABORATORY,  
UNIVERSITY COLLEGE, LONDON.

CLIII.—*The Dissociation Pressures of Alkali Bicarbonates. Part I. Sodium Hydrogen Carbonate.*

By ROBERT MARTIN CAVEN and HENRY JULIUS SALOMON SAND.

IT is the object of the present investigation to study the dissociation pressures of the various alkali bicarbonates in order to discover to what extent the relative stability of each is connected with the basigenic behaviour of its metal, and the position of the latter in the periodic system. The equilibria which must be investigated for this purpose may be expressed by the equation:



in which M indicates the atom of an alkali metal. This equation represents in its most general form a three-component equilibrium, but, as will be seen in the sequel, it is sufficient for the purpose we have in view to treat it as one derived from the two components  $\text{MHCO}_3$  and  $\text{M}_2\text{CO}_3$ , whereby we limit ourselves to the case in which water and carbon dioxide occur in equimolecular proportions in the gaseous phase.

Exact data connected with the subject are very scarce. In 1835 Rose (*Pogg. Ann.*, 1835, **34**, 158) proved that solutions of sodium and potassium hydrogen carbonates may decompose at the ordinary temperature, yielding the normal carbonate and carbon dioxide, and the same conclusion has been arrived at in different ways by several other experimenters (Magnus, *Pogg. Ann.*, 1837, **40**, 590; Marchand, *J. pr. Chem.*, 1845, **35**, 389; Treadwell and Reuter, *Zeitsch. anorg. Chem.*, 1898, **17**, 202).

Corresponding results for solid sodium hydrogen carbonate were obtained by Gautier in 1876, when temperatures above 35° were employed (*Ber.*, 1876, **9**, 1434). In connexion with his work on the solubilities of alkali bicarbonates, Dibbitts, in 1874, determined approximately the partial pressure of carbon dioxide which was in equilibrium with saturated solutions of the respective salts at various temperatures (*J. pr. Chem.*, 1874, [ii], **10**, 440). Lescocier, in 1892, attempted to measure the dissociation pressure of solid sodium hydrogen carbonate between 55° and 100°, but does not appear to have obtained a true equilibrium, since the recorded results are very much lower than ours (*Ann. Chim. Phys.*, 1893, [vi], **28**, 423). Lastly, McCoy, in 1903, carefully studied the equilibrium at 25° between a solution containing sodium carbonate and sodium hydrogen carbonate and a gaseous phase composed of air, carbon dioxide, and water vapour (*Amer. Chem. J.*, 1903, **29**, 437).

## EXPERIMENTAL.

*Method and Apparatus.*—The experiments which we have carried out consist in determining the vapour pressures produced on heating a mixture of sodium hydrogen carbonate and anhydrous sodium carbonate. It is not a priori clear whether only the phases, anhydrous sodium carbonate, sodium hydrogen carbonate, and vapour, will be thus produced, or whether sodium carbonate monohydrate will also be formed, so that the four phases, anhydrous sodium carbonate, sodium carbonate monohydrate, sodium hydrogen carbonate, and vapour, corresponding with a three-component equilibrium, will be present.

If the former is the case, the partial pressure of the water vapour in the gaseous phase will be smaller than the vapour pressure of sodium carbonate monohydrate; and the combined pressures of carbon dioxide and water, which are equal, will be less than twice as great as the dissociation pressure of the monohydrate.

If the latter is the case the partial pressure of the water vapour will be equal to the vapour pressure of sodium carbonate monohydrate, and the partial pressure of the carbon dioxide greater than that of the water vapour, because some water will have been removed from the gaseous phase to form the monohydrate.

The total observed pressure due to carbon dioxide and water vapour will thus be more than twice as great as the vapour pressure of sodium carbonate monohydrate.

A comparison of the vapour pressure of sodium carbonate monohydrate with that of sodium hydrogen carbonate will therefore render a decision between the two alternatives possible; and actual measurements have proved that sodium carbonate monohydrate does not exist in the equilibrium mixture under the conditions of our experiments.

The method of working consisted in heating the mixture of sodium carbonate and sodium hydrogen carbonate in an evacuated flask contained in a thermostat. The vapour generated was accurately balanced against some air, the pressure of which was adjustable, a small gauge consisting of a U-tube containing mercury, which was sealed to the flask, and was also contained in the thermostat, serving as the zero instrument.\* The pressure was then read on a manometer.

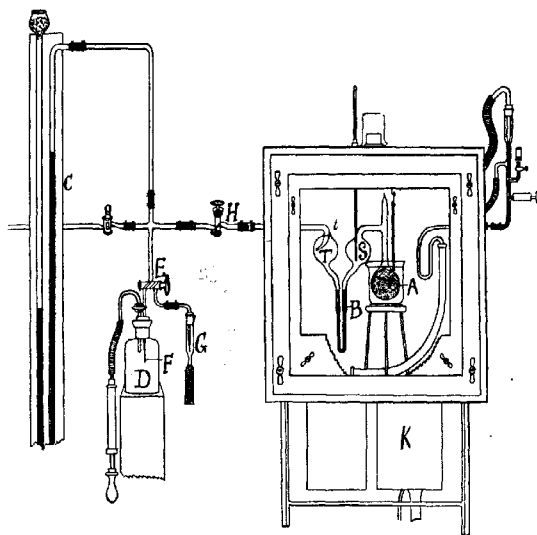
The apparatus was arranged so that it could be laid on its side

\* Since these experiments were begun a very similar method for the measurement of vapour pressures has been described by Johnston (*Zeitsch. physikal. Chem.*, 1908, 62, 333).

without disconnecting during evacuation. Two special bulbs were provided for holding the mercury during this operation.

Fig. 1 shows the apparatus. *A* is the flask containing the reaction mixture, *B* the small mercury gauge, and *C* the manometer. *S* and *T* are the two bulbs just referred to. It will be seen that *T* is fitted with a trap *t*, which makes it possible to withdraw gas from the flask through the mercury without risk of allowing the latter to splash into the exit tubes of the apparatus. The bottle *D* can be either evacuated or fitted with compressed air, according as the

FIG. 1.



pressure to be read is smaller or greater than that of the atmosphere. According to the position of the three-way tap *E*, air can be cut off, or either allowed to enter or leave the apparatus very slowly through the capillaries *F* and *G*, thus permitting the levels of the mercury in the gauge *B* to be very accurately adjusted. The tap *H* was added for further convenience in manipulation.

The general construction of the air thermostat will be clear from the figure. As will be seen, it is double-walled, the products of combustion of the gas from the burner passing up the chimney *K* and between the two walls. Each jacket is provided with a remov-

able transparent front. The apparatus is made of sheet iron, and heavily coated with asbestos outside. Wide steel tubes passing through both jackets are fitted where openings are necessary. The regulator is of the Ostwald pattern, and is filled throughout with mercury. The tubes inside the thermostat are of steel, and are attached to those outside, which belong to a glass regulator of a commercial type, by means of a short, thick-walled rubber connexion.

All the steel joints are screwed, and made mercury-tight by means of oil and red lead. It was found that excellent constancy of temperature was obtained by immersing the flask of the tensimeter in a beaker containing slightly diluted sulphuric acid. Mechanical stirring of the air of the thermostat was tried, but discarded, as it did not improve the results. The temperature of the sulphuric acid was constant to  $0.2^{\circ}$ . It was read on a small, carefully calibrated Anschütz thermometer.

After the gauge had been charged with mercury and the flask with the reaction mixture, the latter was sealed off, and the necessary rubber connexion made. Thick-walled rubber tubing was employed, which was wired on and covered with shellac varnish; thus an air-tight joint was obtained. The tensimeter was then laid horizontally, so that the mercury ran into the bulbs; the apparatus could then be completely evacuated by employing first a water-pump, and then a Sprengel mercury-pump. After the tensimeter had been turned into the upright position, and the thermostat closed, the determination was begun.

Two principal difficulties were encountered in the course of the research. The first consists in obtaining a gaseous phase of equimolecular proportions of water-vapour and carbon dioxide. It is clear from the general laws of chemical equilibrium that if either molecular species were in excess, owing either to selective absorption of the other by the walls of the vessel, or to the presence of adsorbed water in the reaction-mixture or the apparatus, a too high result would be obtained for the decomposition pressure. The second difficulty was due to retardation in the establishment of equilibrium, and was doubtless the result of impermeable crusts formed on the reaction mixture.

We tried to meet the first difficulty by very carefully drying the apparatus before use, gently igniting the sodium carbonate, and leaving the sodium hydrogen carbonate in a desiccator over sulphuric acid for a considerable time before mixing it with the sodium carbonate. A transparent silica vessel was also tried. It was finally found necessary, however, to withdraw large quantities of gas evolved from the reaction mixture at high temperature, and

to continue the process of withdrawal until the readings obtained after two successive withdrawals were identical. The use of the silica vessel was abandoned in the later experiments.

The second difficulty gave a very great deal of trouble, and may very probably be the cause that the results here recorded have been hitherto unknown.

In order to obtain satisfactory readings, it was found necessary to take an amount of sodium hydrogen carbonate which was approximately five hundred-fold that theoretically required to evolve the necessary volume of gas at the highest pressure reached in the experiments. The excess of carbonate sufficient for the re-absorption of the gases on cooling was much smaller than this, an approximately fifty-fold value being sufficient. It is clear that retardation, owing to the formation of crusts, will cause the results to be too low when the temperature is being raised, and too high when it is being lowered. The results will be correct when the same value is obtained in both cases. It was thus found that only from 95° onwards could correct values be obtained on raising the temperature; and in the case of the lowest of these about ten days were necessary for the complete establishment of equilibrium.

On lowering the temperature constant readings were obtained much more rapidly. There is little doubt, moreover, that the numbers obtained in the latter case are substantially correct to about 85°, since they lie on the curve extrapolated from readings taken at higher temperatures.

The rate at which the reaction-mixture was heated was also found to have an effect, rapid heating tending to prevent retardation; the retardation was greatest after all trace of excess of water had been removed as described above.

#### *Sodium Carbonate Monohydrate.*

Table I gives the results obtained for the vapour pressure of sodium carbonate monohydrate. This salt was prepared by heating sodium carbonate decahydrate in a shallow dish on the water-bath until the mass had just become solid again after fusion. The product, after thorough mixing, contained 14.3 per cent. of water, instead of 14.45 according to theory.

A mixture of 40 grams of this salt with 4 grams of the anhydrous carbonate was employed in the experiment.

TABLE I.

<i>Temp. rising.</i>			<i>Temp. falling.</i>		
Temp.	Pressure mm. Hg.		Temp.	Pressure mm. Hg.	
	Observed.	Calculated.		Observed.	Calculated.
30.5°	7.9	8.7	92.7°	419.9	418.0
40.4	15.9	17.9	86.4	297.1	301.0
51.0	36.6	36.9	80.3	216.1	216.0
57.1	53.6	54.6	70.1	121.7	121.0
66.4	98.2	96.8	60.5	69.4	67.5
76.4	166.6	173.0	50.2	39.2	34.9
83.1	243.4	251.0	41.1	23.0	18.8
90.3	363.4	369.0	30.9	13.1	9.0
97.7	539.1	540.0	17.5	6.7	3.1

As is well known, the results of vapour-pressure experiments may be expressed with a considerable degree of accuracy by a formula of the type:

$$\log p = a - \frac{b}{T} \quad . \quad . \quad . \quad (1),$$

in which  $p$  is the vapour pressure,  $T$  the absolute temperature, and  $a$  and  $b$  are constants;  $b$  is connected with the heat of reaction  $q$  per gram-molecule of gas produced, by the formula:

$$q = \log_e 10 R b \quad . \quad . \quad . \quad (2),$$

in which the gas constant  $R$  equals 2 calories per gram-molecule per degree, and  $\log_e 10 = 2.30$ .

In the third column of table I values of  $p$  are calculated from equation (1) by making  $a = 10.825$ ;  $b = 3000.0$ . It will be seen that the majority of the observed values agree closely with the calculated ones, the numbers obtained on raising the temperature being generally very slightly lower, and those found on lowering it, very slightly higher than the calculated values. The curve for sodium carbonate monohydrate is shown in Fig. 2.

#### *Sodium Hydrogen Carbonate.*

Table II contains a complete series of determinations of the decomposition pressure of sodium hydrogen carbonate.

A mixture of 50 grams of sodium hydrogen carbonate and 5 grams of sodium carbonate was taken, the constituents being dried separately in the manner described above, and then mixed. The same mixture was heated and cooled repeatedly for the purpose of obtaining the numbers given, as will be clear from the table.

The approximate quantities of gas withdrawn at various times and temperatures are shown. As will be readily understood, a knowledge of these quantities could be gained by a simple calculation, after withdrawing the gas into the bottle  $D$  (Fig. 1), of known

capacity (600 c.c.), and noting the pressure in the latter before and afterwards. It should be mentioned here that the fact that no air leaked in while gas was being withdrawn past the mercury has been proved repeatedly by cooling the apparatus to atmospheric temperature, and noticing that the pressure ultimately fell practically to zero.

The calculated values have been derived from equation (1) after making  $a=11.8185$  and  $b=3340$ . It will be seen that at high temperatures the agreement is fairly close throughout, the experimental numbers obtained on lowering the temperature being usually slightly higher, and those found on raising it slightly lower than the calculated values. Those numbers which have obviously been considerably vitiated by "retardation" are enclosed in brackets.

Table III gives the results of some earlier experiments, which will be found in the main to confirm those of table II. The

TABLE II.

Series.	Temp.	Pressure in mm. of mercury.			Approx. vol. of gas withdrawn.
		Observed.		Calculated.	
		Rising.	Falling.		
(I.)	90.0°	—	—	—	38 c.c.
	92.4	467.5	—	478.0	—
	104.1	—	936.6	915.0	—
	97.1	—	633.5	625.5	—
	89.6	—	(426.5)	405.0	—
	43.7	—	(51.2)	19.0	—
	—	—	—	—	—
(II.)	107.0	—	—	—	38 c.c.
	108.4	1153.5	—	1151.4	—
	101.9	—	821.9	811.3	—
	92.0	—	473.3	465.1	—
	75.2	—	(210.5)	168.3	—
	49.9	—	(70.6)	29.7	—
	—	—	—	—	—
(III.)	105.0	—	—	—	56 c.c.
	114.4	1594.8	—	1574.0	—
	112.4	—	1413.5	1420.0	—
	107.8	—	1106.7	1116.0	—
	101.2	—	776.2	781.0	—
	93.3	—	507.3	502.0	—
	84.1	—	308.8	292.0	—
	41.5	—	(30.1)	16.0	—
	—	—	—	—	—
(IV.)	88.2	(153.9)	—	499.0	—
	95.8	567.7	—	578.0	—
	95.8	—	—	—	49 c.c.
	95.8	583.4	—	578.0	—
	102.8	836.5	—	853.0	—
	101.4	—	790.8	790.0	—
	101.4	—	—	—	31 c.c.
	101.8	808.6	—	807.5	—
	106.4	1033.2	—	1035.4	—
	107.4	1102.1	—	1093.0	—
	106.6	—	1043.6	1046.7	—



TABLE III.

		Pressure in mm. of mercury.			
		Observed.			Approx. vol. of
Series.	Temp.	Rising.	Falling.	Calculated.	gas withdrawn.
(I.)	107.4°	1097.6	—	1092.2	—
	111.7	1391.7	—	1369.0	—
	111.7	—	—	—	Large unknown vol.
	111.7	—	—	1631.0	—
	115.1	1662.9	—	1633.0	—
	111.9	—	1391.7	1109.0	—
	107.7	—	1111.9	843.0	—
	102.6	—	847.1	680.0	—
	98.7	—	691.7	468.0	—
	92.1	—	485.6	317.5	—
85.5	—	(350.7)	0.8	—	
7.5	—	(2.3)	—	—	
(II.)	110.9	1422.1	—	1313.3	—
	110.9	—	—	—	271 c.c.
	114.3	1642.2	—	1585.7	—
	106.9	1118.6	—	1063.5	—
	106.9	—	—	—	51 c.c.
	107.6	1130.8	—	1103.8	—
	107.6	—	—	—	39 c.c.
	107.6	1098.0	—	1103.8	—
	107.6	—	—	—	35 c.c.
	107.3	—	1091.0	1086.0	—
	105.0	—	978.5	960.0	—
	111.7	1399.2	—	1369.0	—
	115.5	1646.9	—	1664.2	—
	111.2	—	1325.7	1333.5	—
	108.4	—	1165.9	1151.0	—
	104.3	—	937.4	925.0	—
	99.4	—	743.0	707.0	—
	93.6	—	(570.1)	510.0	—
	19.4	—	(11.2)	2.5	—

amounts of substance taken for the determinations were 40 and 4 grams of sodium hydrogen carbonate and sodium carbonate respectively in series (i), and 50 and 5 grams respectively in series (ii).

The dissociation pressure curve of sodium hydrogen carbonate is shown in Fig. 2, together with that of sodium carbonate monohydrate. The curves themselves correspond with the equations, the observed values being indicated in the following manner:

⊙ = temp. rising; × = temp. falling.

It can be shown readily that if the equations derived from our experiments hold for the vapour pressures of sodium carbonate monohydrate and sodium hydrogen carbonate respectively, then the values of the former will be more than half as great as those of the latter at all temperatures below 218°; and that there is thus no possibility of the four-phase equilibrium: anhydrous sodium carbonate, sodium carbonate monohydrate, sodium hydrogen

carbonate, vapour, having been produced in our experiments (see p. 1360).

The vapour pressure corresponding with this four-phase equilibrium may now be calculated. Indicating this pressure at any temperature by  $p$ , the corresponding partial pressures of the water vapour and carbon dioxide by  $p'$  and  $p''$  respectively, we have:

$$p = p' + p''.$$

The quantity  $p'$  is the same as the dissociation pressure of sodium carbonate monohydrate, and may be obtained from the equation we have given for the latter.

The values of  $p''$  may be derived as follows:

If we indicate the dissociation pressure of sodium hydrogen carbonate as obtained by the equation derived for it above by  $p_1$ , then the partial pressure of the water vapour and of the carbon dioxide may each be taken as  $p_1/2$ , and by applying the law of mass action we find:

$$p'' = \frac{\left(\frac{p_1}{2}\right)^2}{p}$$

In this way the values given in table IV have been arrived at. The corresponding numbers for the three-phase equilibrium at the same temperature, which are always a little lower, are given for comparison. The curve for the four-phase equilibrium is also shown in Fig. 2. An attempt was made to verify these numbers experimentally with a mixture of 20 grams of sodium hydrogen carbonate, 15 grams of sodium carbonate monohydrate, and 10 grams of anhydrous sodium carbonate; but the retardation in the pressure values was so great that the experiment was abandoned.

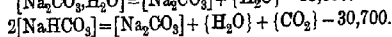
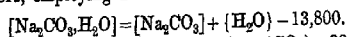
TABLE IV.

*Pressure in mm. of Mercury.*

Temp.	Four-phase equilibrium.			Three-phase equilibrium.
	H <sub>2</sub> O.	CO <sub>2</sub> .	Total.	
30°	8.4	1.2	9.6	6.2
50	34.4	6.6	40.9	30.0
70	119.9	30.2	150.1	120.4
90	364.0	117.8	481.8	414.3
100	605.4	220.8	826.2	731.1
110	981.8	399.0	1380.8	1252.6

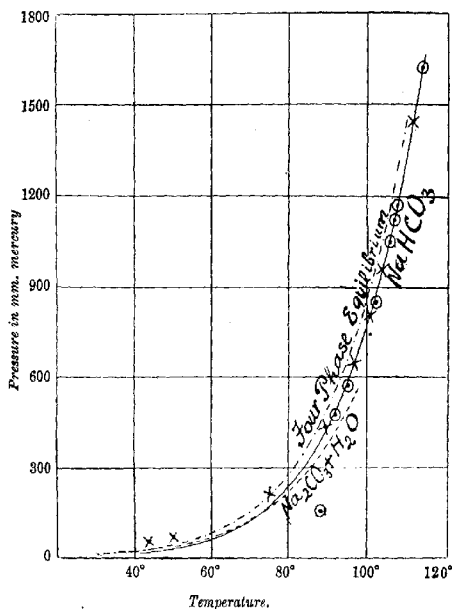
*Heats of Dissociation.*—By applying equation 2, the heats of dissociation per gram-molecule of gas produced are calculated to be: for sodium carbonate monohydrate, 13,800 calories, and for sodium hydrogen carbonate, 15,360 calories.

Therefore, employing Planck's notation, we have:

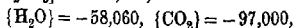
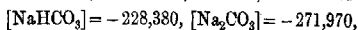


It is interesting to compare the last-named heat-toning with a value for the same reaction derived from direct thermochemical measurements. According to de Forcrand (*Compt. rend.*, 1909, 149, 719), the heats of formation from their elements of 1 gram-

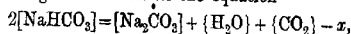
FIG. 2.



molecule of sodium hydrogen carbonate and carbonate are respectively 228,380 and 271,970 calories. Taking the corresponding value for water (as steam at 100°) as 58,060 calories, and for carbon dioxide as 97,000 calories, we have, in Planck's notation:



and substituting these values in the equation



we find  $x=29,700$  calories, instead of 30,700 calories, the figure derived from our experiments.

In view of the indirect nature of the method of comparison, this agreement must be considered quite satisfactory.

*Summary.*

The vapour pressure in mm. of mercury of sodium carbonate monohydrate can be represented with sufficient accuracy by the equation:

$$\log p = 10.825 - \frac{3000.0}{T},$$

that of sodium hydrogen carbonate by the equation:

$$\log p = 11.8185 - \frac{3340}{T}.$$

From the former equation the heat of dissociation of one gram-molecule of sodium carbonate monohydrate is calculated to be 13,800 calories; from the latter, that of two gram-molecules of sodium hydrogen carbonate to be 30,700 calories.

The pressure-values corresponding with the four-phase equilibrium, anhydrous sodium carbonate, sodium carbonate monohydrate, sodium hydrogen carbonate, vapour, have been calculated. They are somewhat higher than the vapour pressure of sodium hydrogen carbonate at all temperatures falling within the range of our experiments.

We take this opportunity of expressing our indebtedness to the Research Fund Committee of the Chemical Society for a grant in aid of this investigation.

UNIVERSITY COLLEGE,  
NOTTINGHAM.

CLIV.—*The Relation of the Velocity of Chlorination of Aromatic Compounds to Constitution. Part I. Chlorination of Anilides.*

By KENNEDY JOSEPH PREVITÉ ORTON and HAROLD KING.

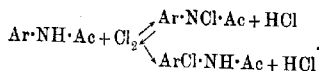
ALTHOUGH it is well known that differences exist in the "readiness" with which anilides are chlorinated or brominated, no systematic study of the relation between the velocities of substitution and constitution has been made.

The investigation is beset with numerous difficulties. The forma-

tion of the compound of hydrogen bromide and bromine:  $\text{HBr} + \text{Br}_2 \rightleftharpoons \text{HBr}_3$ , especially in anhydrous solvents, obscures the process of bromination (*Brit. Assoc. Reports*, 1910, p. 85; Orton and Jones, *Proc.*, 1909, **25**, 305; Jones, this vol., 392). The similar compound of chlorine and hydrogen chloride, if produced at all under analogous conditions, is at such low concentrations as to have no detectable effect on chlorination. Hence we have, in the first place, confined our attention to chlorination.

The process of chlorination is very greatly affected by the medium in which it takes place. For reasons which will appear in what follows, a true comparison of the speeds of chlorination can best be made in glacial acetic acid. Orton and Jones (*Trans.*, 1909, **95**, 1456) have shown that in acetic acid of various dilutions there exists an equilibrium between chlorine, anilide, chloroamine, and hydrogen chloride:  $\text{Ar}\cdot\text{NH}\cdot\text{Ac} + \text{Cl}_2 \rightleftharpoons \text{Ar}\cdot\text{NCl}\cdot\text{Ac} + \text{HCl}$ . In glacial acetic acid the right hand side of the system cannot be detected, but as the medium is diluted, it becomes perceptible; for example, in 95 per cent. acetic acid it forms 20 per cent. of the system; in 75 per cent. acetic acid, 80 per cent.; and finally, in 50 per cent. acetic acid, only a trace of free chlorine is present. These numbers refer to 2:4-dichloroacetanilide, but although in dilute acetic acids there is considerable difference between anilides, in glacial acetic acid the constitution of the anilide has little effect. This equilibrium is attained with extreme rapidity, but in one or two selected instances the velocity of the opposing reactions has been indirectly measured (*Brit. Assoc. Reports, loc. cit.*).

This reversible formation of chloroamine complicates greatly the process of chlorination in the nucleus, *C*-chlorination, in dilute acetic acid. When chlorine is added to an aqueous acetic solution of an anilide which is capable of *C*-chlorination, such as *p*-chloroacetanilide, two reactions, both extremely fast, take place, irreversible *C*-chlorination and reversible *N*-chlorination:

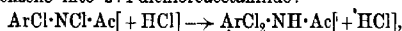


The proportion of the two changes, and hence their relative velocities, can be very easily measured by estimations of the free chlorine (by aspiration) and of the chloroamine (by titration) (Orton and Jones, *loc. cit.*). It varies with the composition of the medium and the constitution of the anilide: thus for *p*-chloroacetanilide, the ratio, *N*-chlorination/*C*-chlorination, in 30 per cent. acetic acid, is 0.93:1; in 50 per cent., 1.25:1; in 65 per cent., 1.55:1, whilst for acetanilide, in the same concentrations of acetic acid, 0.082:1, 0.08:1, and 0.083:1.

The absence of *N*-chlorination, and the fact that *C*-chlorination is slowest in glacial acetic acid, allows of direct measurement of the speeds of *C*-chlorination, and a comparison of different anilides in this medium, which has therefore been chosen for a study of the effect of constitution of anilides.

In selecting a method of experiment, it must be remembered, as shown in the foregoing, that the same velocity of chlorination is found when the reacting system is prepared from chlorine and anilide, or chloroamine and hydrochloric acid, since chloroamines and hydrogen chloride in glacial acetic acid react quantitatively and instantly, forming chlorine and anilide. For a similar reason, as a very convenient way of adding given quantities of chlorine, an anilide, the speed of chlorination of which is under investigation, may be treated with the molecular proportions of hydrogen chloride and some chloroamine, such as acetylchloroamino-2:4-dichlorobenzene, the anilide corresponding with which is not chlorinated in the nucleus at an appreciable rate. This last procedure is in every way to be preferred, for the preparation of standard solutions of chlorine in glacial acetic acid, or the preparation of chloroamines often difficult to purify, is avoided. Moreover, the simplification of the manipulation lessens the opportunity for the introduction of small quantities of water, which has a powerful accelerating effect on the velocity of chlorination. We have put these three methods of operating to a thorough experimental test, and have shown that the value of the velocity coefficient is independent of the procedure, and, further, of the order in which the three reagents are mixed.

The speed of chlorination in glacial acetic acid is independent of the quantity of hydrogen chloride, provided that the acid is in excess of one molecular proportion. When a chloroamine is used as chlorinating agent, and but a relatively small proportion of hydrogen chloride, 1/20—1/10th gram-molecular proportion, added, the concentration of the chlorine in the system remains constant at 1/20—1/10th gram-molecular proportion during the main part of the reaction. Hence the reaction is apparently of the first order. Moreover, since the quantity of chlorine produced in the system is equivalent to the hydrogen chloride added, the speed of chlorination is proportional to the concentration of the acid. When the chlorination is carried out by treatment of the isomeric chloroamine with a small proportion of hydrogen chloride (1/20—1/10th gram-mol.), for example, the conversion of acetylchloroamino-*p*-chlorobenzene into 2:4-dichloroacetanilide:



the speed of chlorination is proportional to the *square* of the concen-

tration of the hydrogen chloride added, for now quantities equivalent to the hydrogen chloride, of both the reacting substances anilide and chlorine, are produced in the system. These relations only hold in glacial acetic acid, for in the diluted media chloroamine and hydrogen chloride can co-exist.

Experiment has shown that hydrogen chloride may be present in excess to the extent of 8—10 molecular proportions without affecting the character or speed of the chlorination. This behaviour is in marked contrast to the effect of hydrogen bromide on bromination (*loc. cit.*); addition of sufficient excess of hydrogen bromide, 4 gram-molecular proportions, will bring the bromination of acetanilide in glacial acetic acid to a standstill.

The reaction is naturally a simple change of the second order. Whatever view be held as to the mechanism of substitution, the first step is the interaction of separate molecules of anilide and chlorine. There appear to be no disturbing effects produced by change of concentration, or during the course of the reaction. Frequently, of course, a chloroanilide is produced in the reaction, which is itself capable of chlorination. Notwithstanding the fact that its concentration exceeds that of the original anilide for the second half of the reaction, the unchlorinated (or less chlorinated) anilide reacts so much more rapidly (about 200 times) with chlorine than the chlorinated anilide that the effect of the consecutive reaction is scarcely perceptible, even towards the end of the change.

*Results: (i) Acyl Groups.*—The formyl group shows its usual influence; the speed of chlorination reaches a maximum with the propionyl group, but falls off very slightly with increasing length of the acyl chain; the branch chain in *isovaler*anilide has an obvious depressing effect on the velocity.

	$k_{11}$		$k_{11}$
Formanilide .....	4.95	Stearanilide .....	64
Acetanilide .....	40	<i>iso</i> Valeranilide .....	57
Propionanilide .....	72	Oxanilide .....	2
Butyranilide .....	64.5	Benzanilide .....	42

(ii) The effect of the presence of chlorine in the ortho- or para-positions respectively is well shown by the following numbers:

	$k_{11}$		$k_{11}$
Acetanilide .....	40	Benzanilide .....	42
<i>o</i> -Chloroacetanilide .....	0.073	<i>p</i> -Chlorobenzanilide .....	0.16
<i>p</i> -Chloroacetanilide .....	0.21		

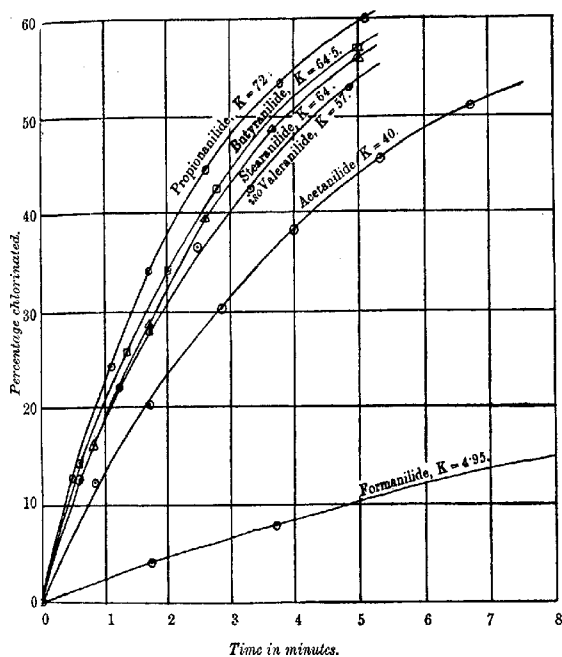
The striking effect of the chlorine atom in the ortho-position is noteworthy. The chlorination of 2:4-dichloroacetanilide in glacial acetic acid cannot be detected at the ordinary temperature; *s*-trichloroacetanilide is produced at 150—160°, but the yield is

poor, as the attack of chlorine on the acetic acid solvent is then considerable.

(iii) Chlorine offers a marked contrast to the methyl group:

	$k_{11}$		$k_{11}$
Acetanilide .....	40	Benzanilide .....	42
Aceto- <i>o</i> -toluidide .....	9	Benzo- <i>o</i> -toluidide .....	5.7
Aceto- <i>p</i> -toluidide .....	77	Benzo- <i>p</i> -toluidide .....	70
<i>p</i> -Chloroacetanilide .....	0.21	<i>p</i> -Chlorobenzanilide .....	0.16

FIG. 1.



The methyl group in the para-position causes an increase in the speed of chlorination; but the influence of position is well shown, in that  $k_{11}$  for the chlorination of aceto-*o*-toluidide is only 1/4th that of  $k_{11}$  for acetanilide.

These numbers give also an opportunity of contrasting the acetyl and benzoyl groups. Although benzanilide is chlorinated slightly more rapidly than acetanilide, in the case of the corresponding

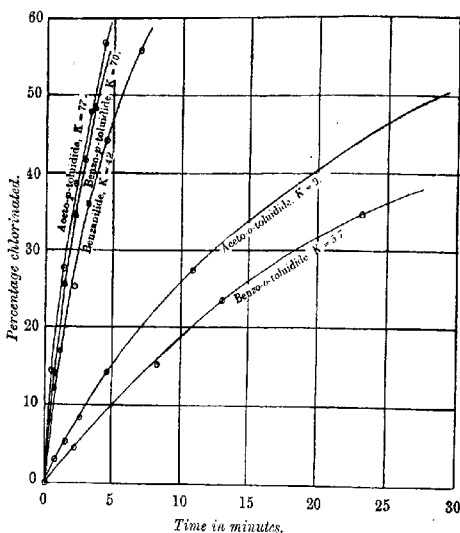


derivatives the acetyl compounds are chlorinated about  $1\frac{1}{2}$  times as fast as the benzoyl compounds.

(iv) Measurements of the chlorination of anisidides and phenetidides show that the mere occupation of the ortho- or para-positions is not a decisive factor. Aceto-*o*-anisidide and aceto-*o*-phenetidide are chlorinated more rapidly than the para-derivatives.

	$k_{11}$		$k_{11}$
Acetanilide .....	40	Aceto- <i>p</i> -toluidide.....	77
Aceto- <i>o</i> -anisidide .....	60	Aceto- <i>o</i> -phenetidide .....	90
Aceto- <i>p</i> -anisidide .....	57	Aceto- <i>p</i> -phenetidide .....	85

FIG. 2.



The ethoxyl group is more favourable to chlorination than the methoxyl; the methyl group occupies an intermediate position.

(v) The cumulative effect of methyl groups is illustrated in the series:

	$k_{11}$		$k_{11}$
Acetanilide .....	40	Aceto- <i>p</i> -toluidide.....	77
Aceto- <i>o</i> -toluidide .....	9	Aceto- <i>p</i> -cumidide .....	630
Aceto- <i>m</i> -xylylide.....	9		

The introduction of a methyl group in the para-position with respect to the group NHAc in aceto-*o*-toluidide, as illustrated in aceto-*m*-xylylide, has no effect, whilst the introduction of an ortho-

methyl group in aceto-*p*-toluidide reduces the value of  $k_{11}$  to 1/9th 77 to 9. The introduction of a third methyl group, as in  $\psi$ -cumi-  
dide, is, however, accompanied by a very large rise in the value of  
 $k_{11}$  from 9 to 630.

(vi) The naphthalides are chlorinated at a very high speed.

	$k_{11}$		$k_{11}$
Acetanilide .....	40	Formanilide .....	4.95
Aceto- $\alpha$ -naphthalide .....	550	Formo- $\alpha$ -naphthalide .....	565
Aceto- $\beta$ -naphthalide .....	"instantaneous chlorination."		

In the case of aceto- $\beta$ -naphthalide at a concentration of  
1/240 gram-molecule per litre, it is impossible to detect free chlorine  
after mixing.

#### EXPERIMENTAL.

The procedure which has been found most suitable in making  
the measurements of the velocity is as follows: A quantity of the  
anilide (0.00041 gram-molecule) is dissolved in about 15 c.c. of  
glacial acetic acid, and placed in a stoppered flask. One molecular  
proportion of acetylchloroamino-2:4-dichloroacetanilide, the source  
of the chlorine, is dissolved in about 85 c.c. of glacial acetic acid  
in a 100 c.c. stoppered measuring flask. Both these solutions are  
allowed to attain the temperature of the bath, 16°. One molecular  
proportion of hydrogen chloride, in the form of the constant boiling  
aqueous (22 per cent.) solution (0.058 c.c.), is then added, from a  
burette graduated to 1/50ths, to the solution of the chloroamine;  
and then the solution of the anilide immediately introduced. The  
total volume of the mixture was as nearly as possible 100 c.c., and  
hence the concentrations of the reacting substances, 0.0041 gram-  
molecule per litre. The reacting solution was carefully shielded  
from light in a closed bath kept in a dark room.

Volumes of 10 c.c. were withdrawn by a pipette at appropriate  
intervals, and added to a 5 per cent. potassium iodide solution;  
the iodine set free was titrated with *N*/50-thiosulphate.

In the case of anilides with a low solubility in glacial acetic  
acid, such as oxanilide and stearanilide, the anilide was dissolved  
in a larger volume of acid, 80–85 c.c., and the chloroamine in  
the smaller volume (20–15 c.c.). These are mixed, and the  
hydrogen chloride added finally.

When the speed was low the concentrations were raised to 0.025  
gram-molecule per litre.

The anilides were either the purest material supplied by Kahl-  
baum or prepared from anilines obtained from the same source.  
They were recrystallised two or three times before use. The  
*o*-chloroaniline was prepared in the laboratory, and purified by

recrystallising the hydrochloride as described in the following paper (this vol., p. 1381).

Two determinations at least were made of the speed of chlorination, and the anilide was always recrystallised again before the second measurement. The values given for  $k_{11}$  in the foregoing are the mean of two concordant experiments.

For the highly dilute solutions which are required for these very speedy reactions, it is essential that the glacial acetic acid should be free from substances which react with chlorine. We used either the special "K" acid supplied by Kahlbaum, or an acid prepared by ourselves by distillation of a good commercial acid from phosphoric oxide. In all cases the acid was shown to be stable to bromine or chlorine (Orton, Edwards, and King, this vol., p. 1178).

Since the speed of chlorination in glacial acetic acid is very sensitive to the addition of water, increasing in a direct ratio, it was very important that the medium should be kept of constant composition throughout the whole series of experiments. We aimed at using an acid melting at  $16.3^{\circ}$ , that is, it contained 0.14 per cent. of water, as such an acid was far easier to obtain than an absolute acetic acid. Moreover, the addition of a trace of water obviously produces far less effect on the velocity than with an absolute acid. The high or irregular speeds which were occasionally observed could generally be ascribed to accidental entrance of small quantities of water during the manipulations.

The following figures are typical examples of the whole series of experiments. Concentrations are 0.0041, except where otherwise stated:

<i>Formanilide.</i>			<i>Acetanilide.</i>		
Time (minutes).	Percentage chlorinated.	$k_{11}$ .	Time (minutes).	Percentage chlorinated.	$k_{11}$ .
5.0	8.8	4.75	0.8	12.3	—
14.3	21.4	4.75	1.7	20.3	40
28.3	33.4	4.75	2.8	30.8	40
40.3	43.5	4.77	4.0	38.2	39
57.6	53.5	5.00	5.3	45.6	39
81.7	62.5	5.10	6.7	51.1	39

<i>Propionanilide.</i>			<i>Stearanilide.</i>		
Time (minutes).	Percentage chlorinated.	$k_{11}$ .	Time (minutes).	Percentage chlorinated.	$k_{11}$ .
0.5	12.9	74	0.8	16.1	63
1.1	24.4	73	1.7	28.6	59
1.7	34.1	72	2.6	39.5	57
2.7	44.5	74	3.7	48.7	57
3.8	53.6	74	5.0	56.0	56
5.1	60.0	73	6.4	62.4	57

*o*-Chloroacetanilide; conc. 0.025.

Time (minutes).	Percentage chlorinated.	$k_{II}$ .
60.0	10.0	0.074
184.1	24.8	0.072
360.1	40.8	0.076
606.2	53.2	0.075
1007.5	65.3	0.074

*p*-Chlorobenzanilide;

Time (minutes).	Percentage chlorinated.	$k_{II}$ .
69.5	5.6	—
179.2	10.6	0.165
361.4	19.3	0.165
575.2	27.8	0.167
851.0	29.8	0.165
871.2	36.6	0.165

We wish to express our indebtedness to the Government Grant Committee of the Royal Society, and to the British Association, for grants which have partly defrayed the cost of this investigation.

UNIVERSITY COLLEGE OF NORTH WALES,  
BANGOR.

CLV.—*Chlorination of Acylanilides. Effect of the Constitution of the Acyl Group on the Proportion of the Ortho- and Para-derivatives.*

By HAROLD KING and KENNEDY JOSEPH PREVITÉ ORTON.

In a previous paper, Jones and Orton (Trans., 1909, **95**, 1056) demonstrated that in the chlorination of acetanilide about 40—46 per cent. of the product was *o*-chloro- and 54—60 per cent. *p*-chloro-acetanilide. This ratio appeared to be independent of the dilution of the acetic acid which was used as solvent, a fact which implies only that the rates of the formation of the two chloro-derivatives bear the same relation to one another in such media.

In this paper we record the effect of varying the acyl group on the proportion of *o*- and *p*-chloro-derivative, and have used form-, propion-, stear-, and benz-anilide.

As the medium, acetic acid, more or less diluted, is alone suitable, for in other (anhydrous) media, chloroform and so forth, considerable quantities of a dichloro-derivative are produced, and consequently a part of the original anilide left unchanged. The cause of this difference is not to be found in a similarity in the velocities of chlorination of unsubstituted anilide and monochloroanilide; the chlorination of the unsubstituted anilide is some two hundred times as fast as that of the *p*-chloro-derivative, which is three to four times as rapid as the chlorination of the *o*-derivative. It is more probable that the formation of the dichloro-derivative is due to the preferential combination of the hydrogen chloride with the unsubstituted anilide, which is thus shielded from the attack of chlorine.

The results are summarised in the following table, where the numbers represent the percentage of the anilide chlorinated, found in the product in one or other form.

	<i>p</i> -Chloro-anilide.	<i>o</i> -Chloro-anilide.	Ratio: <i>o</i> -Chloroanilide, <i>p</i> -Chloroanilide.	2:4-Dichloro-anilide.	Unchanged anilide.
Acetanilide ...	51.0	44	0.89/1	1.2	1.2
Propionanilide	64	26	0.4/1	3.2	3.2
Stearanilide ...	69.5	20.8	0.3/1	2.2	2.2
Benzanilide ...	65.5	11.2	0.17/1	11.1	9.2
Formanilide...	62	3.0	0.048/1	—	—

The loss which is apparent from these figures is to be attributed mainly to the difficulty of estimating with any accuracy the amount of anilide which escapes chlorination.

In the case of formanilide some other reaction takes place simultaneously, which is the more prominent in dilute acetic acid solution, when as much as 75 per cent. of the anilide escapes chlorination; the figures given are for glacial acetic acid.

The *p*-chloroanilide bears the greater proportion of the loss which results from the formation of the dichloro-derivative, since, apart from its greater concentration, the speed of chlorination of the *p*-chloro-compound is two to four times as great as that of the *o*-chloro-compound. Hence the figures for the *p*-chloro-compound are all relatively low.

The numbers in the fourth column express the ratio of the velocities of the formation of the two monochloroanilides. They appear to be independent of the dilution of the acetic acid. It is obvious that the chlorination of acetanilide is the most favourable process for the production of *o*-chloroaniline. The figures show the remarkable position occupied by formanilide; the *o*-chloro-derivative is only formed at 1/20th the rate of the para-derivative.

Omitting formanilide, the effect of the nature of the acyl group on the proportion of the two derivatives belongs to the general "steric" type met with in similar reactions.

#### EXPERIMENTAL.

The method of estimating the proportion of *o*- and *p*-chloroacylanilides is generally the same as that used for acetanilide by Jones and Orton (*loc. cit.*). A solution of anilide in glacial acetic acid is treated with that quantity of bleaching powder solution which will give one molecular proportion of chlorine. The solid which separates is collected, and when possible the proportion of *o*- and *p*-chloro-derivatives estimated from the melting point. A second separation is obtained by dilution to 20 or 10 per cent. acetic acid. This last mother liquor, which often contains much of the ortho-

derivative, is either strongly acidified, boiled to hydrolyse the anilide, and then, after removal of the mineral acid with alkali or sodium acetate, distilled in steam, when the anilines pass over; or it is extracted with chloroform, and the anilide thus obtained hydrolysed with aqueous sulphuric acid.

The different chloroanilines are separated by distilling from 1 per cent. sulphuric acid, when the *o*-chloro- and the 2:4-dichloro-compounds pass over, leaving *p*-chloroaniline and aniline in the acid mother liquor. They are subsequently distilled, after rendering the liquid alkaline. The *o*- and *p*-chloroacylanilide in the separations from the original acetic acid liquors are treated in the same way, when the melting-point curve of the mixture is not available for the estimation.

The 2:4-dichloroaniline is separated from the *o*-chloro-compound by fractional precipitation from solutions of the hydrochlorides as previously described (*loc. cit.*). For weighing, it is generally simplest to convert the anilines into acetyl derivatives by evaporation on the water-bath with a little acetic anhydride in tared glass dishes. In the following, some of the final and more successful experimental results are given.

*Formanilide*:—Treatment of the glacial acetic acid solution with bleaching powder solution produced a coloured liquid, which darkened on warming. Only 25 per cent. of the anilide could be recovered by the method above described.

The loss was greatly decreased (to 25 per cent.) when the anilide was treated with a standard solution of chlorine in glacial acetic acid. After neutralising with sodium carbonate, the acetic acid was completely distilled off under diminished pressure. The remaining anilides were hydrolysed, and the anilines separated.

*Propionanilide*:—Ten grams of propionanilide in 150 c.c. of glacial acetic acid were treated with one equivalent of bleaching powder solution, and finally diluted to 10 per cent. acetic acid, when 6.8 grams separated. Extraction with chloroform yielded an additional 6.5 grams. The total solid was hydrolysed, and the anilines separated with the following result:

Propionanilide recovered as <i>p</i> -chloroacetanilide.....	6.4 grams
“ “ “ <i>o</i> -chloroacetanilide.....	2.57 “
“ “ “ 2:4-dichloroacetanilide.....	0.32 “
“ “ “ acetanilide.....	0.32 “
“ “ “ Loss.....	0.39 “

*Benzanilide*:—Owing to the sparing solubility, 500 c.c. were required for 10 grams. The main quantity of chlorinated anilides separated on dilution to 50 per cent., and the proportion of *o*- and *p*-chloro-derivatives was estimated from the melting-point curve. The

material remaining in solution was recovered and analysed as described in the foregoing.

Benzanilide recovered as <i>p</i> -chloroacetanilide .....	6.54 grams
" " " <i>o</i> -chloroacetanilide .....	1.11 "
" " " 2:4-dichloroacetanilide .....	1.11 "
" " " acetanilide.....	0.92 "
Loss.....	0.32 "

*Stearanilide*:—The anilide, which was prepared by heating stearic acid with excess of aniline at 280—300° for five hours, is so sparingly soluble that 600 c.c. of glacial acetic acid are required for 5 grams at 40°. The separation of unchlorinated anilide during the addition of the bleaching powder can be avoided by using a concentrated solution of the latter. There was some difficulty experienced in hydrolysing the anilides, many hours' boiling with aqueous alcoholic sulphuric acid being necessary.

Neither *o*- nor *p*-chlorostearanilide has hitherto been described. Two grams of stearanilide dissolved in 300 c.c. of glacial acetic acid were treated with the calculated quantity of concentrated bleaching powder solution. A solid separated, which melted at 94—99°. Repeated crystallisation from acetic acid raised the melting point to 101—102°. *p*-Chlorostearanilide forms feathery needles, which gave on analysis the following numbers:

0.2760 gave 0.0978 AgCl. Cl=8.8.

$C_{24}H_{40}ONCl$  requires Cl=9.0 per cent.

On hydrolysis, *p*-chloroaniline was obtained.

The mother liquor from the above was diluted to 50 per cent. acetic acid, whereupon a solid, melting at 60—65°, separated. Repeated crystallisation from alcohol raised the melting point to 67—68.5°. *o*-Chlorostearanilide forms needles:

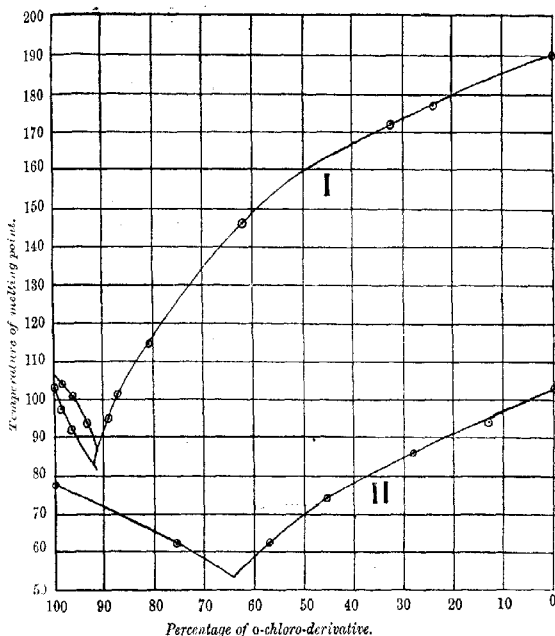
0.2082 gave 0.737 AgCl. Cl=8.8 per cent.

$C_{24}H_{40}ONCl$  requires Cl=9.0 per cent.

*Preparation of o-Chloroaniline*:—As a result of our experience, we find that *o*-chloroaniline is best prepared and purified in the following way. One hundred grams of acetanilide dissolved in 1 litre of glacial acetic acid are treated with one equivalent of bleaching powder solution. After keeping for fifty hours, the solid is collected, and recrystallised once more from alcohol, 50 grams of pure *p*-chloroacetanilide being obtained.

The alcoholic and acetic acid mother liquors contain the *o*-chloroacetanilide, together with 5—10 per cent. of the *p*-chloro-compound. The alcoholic mother liquor is evaporated to dryness, and the acetic acid liquor diluted to 5 per cent., and extracted with chloroform. The mixed solids are hydrolysed with 10 per cent.

aqueous sulphuric acid, and the solution diluted to 1 per cent. acid and distilled in steam. The *o*-chloroaniline which passes over, with a small quantity of the para-compound, is collected with chloroform, and dissolved in warm 10 per cent. hydrochloric acid, using 11 c.c. of acid for each gram of *o*-chloroaniline. The hydrochloride of the *o*-chloro-derivative separates on cooling, and can be again recrystallised in the same way. The purity can be tested by the



melting point of the acetyl derivative. In this way a far better yield of purer material can be obtained than by crystallisation of the picrate from alcohol or the acetyl derivative from petroleum.

*Melting-point Curves of Mixtures of o- and p-Chlorobenz- and o- and p-Chloroformanilides.*

The figure shows the form of the two curves: I is benzanilide, and II formanilide. As in the case of the corresponding acet-



anilides (Jones and Orton, *loc. cit.*), it will be seen that a part of the chlorobenzanilide curves is duplicated; here, however, it occurs when the *o*-chloro-derivative is in excess, whereas in the case of the acetyl derivatives the *p*-chloro-compound was in excess.

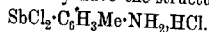
UNIVERSITY COLLEGE OF NORTH WALES,  
BANGOR.

CLVI.—*Aromatic Antimony Compounds. Part II.*  
*The Action of the Chlorides of Antimony on*  
*Aniline and its Derivatives.*

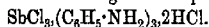
By PERCY MAY.

WHEN antimony trichloride reacts with aniline, the only organic compounds obtained contain three aromatic residues to one atom of antimony, and compounds such as *p*-aminophenyldichlorostibine,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SbCl}_2$ , which might yield *p*-aminophenylstibic acid,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SbO}_3\text{H}_2$ , by hydrolysis and oxidation, do not appear to be formed. Breinl and Nierenstein, however (*Ann. Tropical Med.*, 1909, 2), claim to have obtained both the *m*- and *p*-acids by this method. As the account of their work contains very obvious inaccuracies, and as no traces of these compounds could be obtained by a careful repetition of their experiments, it must be concluded that these investigators were mistaken in their conclusions.

It was found that whereas antimony trichloride combines with three molecules of aniline, it combines with only one molecule of toluidine or chloroaniline, and does not combine with nitroaniline under the experimental conditions employed. The compounds formed are hydrolysed by water, and are probably of an additive nature. The structure  $\text{Sb}(\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{HCl})_3$  is unlikely, for although the entrance of an amino-group into each aromatic radicle would probably reduce the stability of triphenylstibine, yet the latter is so very stable (*Trans.*, 1910, 97, 1956) that it is improbable that the amino-derivative would be so readily hydrolysed. On the other hand, the mono-aryl derivatives, such as  $\text{C}_6\text{H}_5\cdot\text{SbCl}_2$ , are less stable, and this fact, together with the somewhat greater stability of the derivatives of toluidine compared with those of aniline, renders it possible that the former may have the structure:



By heating aniline and antimony trichloride at a higher temperature, a substance is formed having the composition



This compound is somewhat more stable than the compound  $\text{SbCl}_3 \cdot (\text{C}_6\text{H}_5 \cdot \text{NH}_2)_3$ , obtained at a lower temperature, although it decomposes into antimony chloride and aniline hydrochloride when it is warmed with hydrochloric acid.

Antimony pentachloride reacts violently with most aromatic compounds. In all the cases that have been investigated, partial chlorination of the aromatic compound takes place, the remainder then forming additive products with the antimony trichloride set free. This explains the value of antimony trichloride as a catalytic agent in the chlorination of organic compounds.

#### EXPERIMENTAL.

##### *Action of Antimony Trichloride on Aniline.*

On mixing equal quantities of aniline and antimony trichloride, heat is evolved, and combination ensues. The compound formed is readily soluble in hot aniline, from which, on cooling, it crystallises in needles. If the excess of aniline is removed by washing with an inert solvent, such as ether or light petroleum, the crystals are destroyed, and therefore these appear to contain aniline of crystallisation.

This compound was obtained in the pure state by the following method. Sixteen grams of aniline were warmed on the water-bath with 10 grams of antimony trichloride for a quarter of an hour; the product was extracted with hot benzene, and the solution filtered. The residue was washed with alcohol, and dried in a vacuum (I), and from the filtrate white needles separated, which were dried on a porous plate and then in a vacuum (II).

The antimony was estimated by dissolving in hydrochloric acid, and precipitating as sulphide in the usual way. The chlorine, except where otherwise indicated, was estimated by boiling with dilute nitric acid and excess of standard silver nitrate, the excess of silver being then determined by means of thiocyanate.

Crops I and II were found to have the same composition:

Found: Sb=23.79, 23.80; Cl=21.13.

$\text{SbCl}_3 \cdot (\text{C}_6\text{H}_5 \cdot \text{NH}_2)_3$  requires Sb=23.76; Cl=21.00 per cent.

This substance could be obtained more readily by adding a slight excess of aniline to a solution of antimony trichloride in benzene until the precipitate first formed just redissolved. Part of the solvent was evaporated, and the solid residue separated and extracted with light petroleum to remove all free aniline. The

white product thus obtained was recrystallised from alcohol, and obtained in needles. (Found: Sb=23.53; Cl=21.4.)

Trianiline antimony trichloride melts and decomposes at 130—170° (Schiff, *Ber.*, 1901, **34**, 805, gives 80°), is hydrolysed by water or alkali, and dissolves readily in hydrochloric acid, less readily in other mineral acids, giving the reactions of the corresponding salts of aniline and of antimony.

On boiling with 90 per cent. alcohol and filtering, the filtrate, on evaporation, yielded crystals of aniline hydrochloride, which were identified by analysis and by their melting point, indicating that the substance had been hydrolysed under these conditions. Aqueous ammonium carbonate decomposes the substance, with liberation of aniline and antimony trioxide.

*Action of Aniline on Antimony Trichloride at a Higher Temperature.*

Forty grams of antimony trichloride were heated to 210°, and 40 grams of aniline added in small portions at a time, the mixture being kept boiling for half an hour. When cooled to about 80°, the product was poured into cold water, and the purple precipitate collected, washed, and extracted with alcohol. From the alcoholic extract almost colourless crystals were obtained, which dissolved in hydrochloric acid, giving solutions which could be diazotised, and which gave an orange precipitate with hydrogen sulphide. The substance behaves, therefore, like an additive product of antimony trichloride and aniline:

0.1495 gave 0.2063 CO<sub>2</sub> and 0.0651 H<sub>2</sub>O. C=37.62; H=4.35.

0.1760 „ 0.2146 AgCl; Cl=30.94.

SbCl<sub>3</sub>.(C<sub>6</sub>H<sub>5</sub>.NH<sub>2</sub>)<sub>3</sub>.2HCl requires C=37.3; H=4.0;

Cl=30.65 per cent.

This compound forms colourless crystals, which dissolve in hot alcohol, and are insoluble in, and almost unchanged by, water. They melt and decompose at 170—175°.

*Action of Antimony Trichloride on o-Toluidine.*

o-Toluidine was added to a benzene solution of antimony trichloride, and the product treated in just the same way as described in the case of aniline:

Found: Cl=51.95, 31.56; N=4.88.

SbCl<sub>3</sub>.C<sub>6</sub>H<sub>4</sub>Me.NH<sub>2</sub> requires Cl=31.84; N=4.20 per cent.

o-Toluidine antimony trichloride crystallises from alcohol in long, colourless needles, which melt sharply at 148°, without any decom-

position. It resembles trianiline antimony trichloride in its behaviour towards hydrochloric acid, nitrous acid, and ammonium carbonate. It is not, however, hydrolysed by boiling with 90 per cent. alcohol.

*Compound of p-Toluidine and Antimony Trichloride.*

This compound was prepared in the same manner as that derived from *o*-toluidine, which it resembles in its chemical character, but does not crystallise so well, and does not melt without decomposition.

*p*-Toluidine antimony trichloride forms colourless crystals, which decompose above 120°:

Found: Cl=31.12; N=4.42.

$\text{SbCl}_3 \cdot \text{C}_6\text{H}_4\text{Me} \cdot \text{NH}_2$  requires Cl=31.84; N=4.20 per cent.

*Compound of p-Chloroaniline and Antimony Trichloride.*

On mixing benzene solutions of antimony trichloride and *p*-chloroaniline, a precipitate was formed, which did not redissolve in excess of either of the reagents. The precipitate was collected, and washed with benzene and alcohol, in both of which solvents it is practically insoluble:

Found: N=3.49; Cl(ionisable)=31.0.

$\text{SbCl}_3 \cdot \text{C}_6\text{H}_4\text{Cl} \cdot \text{NH}_2$  requires Cl=30.2(ionisable); N=3.98 per cent.

*p*-Chloroaniline antimony trichloride is a white powder, practically insoluble in all the usual organic solvents, and melts with some decomposition at 160—165°. In its chemical behaviour it resembles the corresponding toluidine derivatives.

*m*-Nitroaniline and *p*-nitroaniline do not combine with antimony trichloride under the above-described experimental conditions.

*The Action of Antimony Pentachloride on Benzene, Aniline, etc.*

The action of antimony pentachloride on benzene is very violent. Charring takes place, hydrogen chloride is evolved, and crystals of an additive compound separate; the action of antimony pentachloride on toluene and xylene is similar. In the case of aniline the action is almost explosive in its violence, and is best controlled by dissolving both the reacting substances in chloroform, one of the few organic solvents with which antimony pentachloride does not vigorously react. Even then, on slowly adding a chloroform solution of antimony pentachloride to one of aniline, the reaction is very vigorous, and so much charring takes place that it was not possible to isolate any compound in a pure condition. A chloroform solution of antimony pentachloride on evaporation leaves crystals

of an additive compound, which was too unstable for analysis losing chloroform when the vapour pressure of the latter falls below a certain point. When exposed to moist air it gave the vitreous antimonie oxychloride described by Anschütz and Evans.

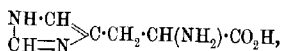
I wish to express my thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed most of the expenses of this investigation.

UNIVERSITY COLLEGE, LONDON.

### CLVII.—*The Synthesis of Histidine.*

By FRANK LEE PYMAN.

In the following paper an account is given of the synthesis of histidine (*l*- $\alpha$ -amino- $\beta$ -glyoxaline-4(or 5)-propionic acid), and it may be of interest, in the first place, to recall that this amino-acid is

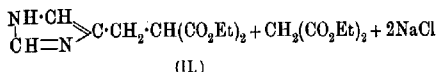
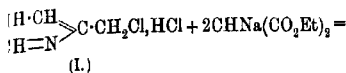


Histidine.

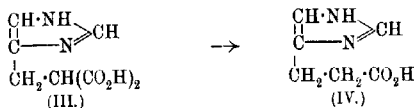
a compound of considerable biochemical importance, since it occurs as a degradation product of nearly all albumins, and notably in large amount by the hydrolysis of hæmoglobin. It was first discovered by Kossel (*Zeitsch. physiol. Chem.*, 1896, **22**, 176), and its constitution was determined mainly by the work of Fränkel (*Monatsh.*, 1903, **24**, 229), Paul (*Zeitsch. physiol. Chem.*, 1904, **42**, 513), and Knoop and Windaus (*Beitr. chem. Physiol. Path.*, 1905, 7, 144).

In a recent communication (this vol., p. 668) the preparation of certain glyoxaline derivatives was described. It was shown that 4(or 5)-chloromethylglyoxaline (I) is a highly reactive compound, the chlorine atom in the side-chain being readily replaced by hydroxyl under the influence of hot water, and by the cyano-group through the agency of aqueous potassium cyanide at 0°. It therefore seemed probable that this salt could be condensed with compounds of the type of ethyl sodiomalonate, forming the corresponding glyoxalinemethyl  $\text{C}_3\text{H}_5\text{N}_2\cdot\text{CH}_2$ , derivatives, and this proved to be the case. On adding one molecule of this salt to two molecules of ethyl sodiomalonate, ethyl 4(or 5)-glyoxalinemethylmalonate

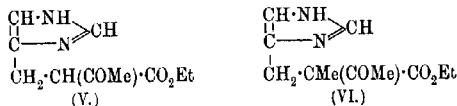
(I) was formed in a yield amounting to 49 per cent. of the theoretical:



This ester, on hydrolysis with barium hydroxide, gave the corresponding acid, 4(or 5)-glyoxalinemethylmalonic acid (III), together with a certain amount of  $\beta$ -glyoxaline-4(or 5)-propionic acid (IV), produced from the former by the removal of carbon dioxide. 4(or 5)-Glyoxalinemethylmalonic acid is a beautifully crystalline compound, which, on heating, loses carbon dioxide at  $180^\circ$ , and is converted into  $\beta$ -glyoxaline-4(or 5)-propionic acid (IV), a substance which has previously been prepared by Knoop and Windaus (*Beitr. chem. Physiol. Path.*, 1905, 7, 144), both by the degradation of histidine, and synthetically from glyoxylpropionic acid:



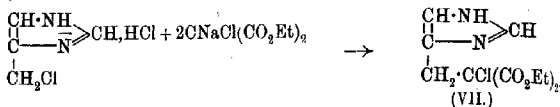
Similar condensation products were obtained by the action of 4(or 5)-chloromethylglyoxaline hydrochloride on ethyl sodioacetoacetate and ethyl sodiomethylacetoacetate, *ethyl* 4(or 5)-glyoxalinemethylacetoacetate (V) and *ethyl* 4(or 5)-glyoxalinemethylmethylacetoacetate (VI) being formed:



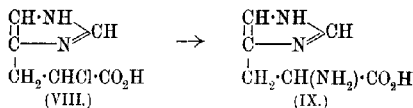
In view of these results, it seemed of interest to attempt the condensation of this salt with ethyl sodiochloromalonate, since this might lead to a synthesis of histidine, for Conrad (*Annalen*, 1881, 209, 241) has shown that this ester condenses with benzyl chloride, forming ethyl benzylchloromalonate, although it does not condense with less reactive alkyl chlorides.

On experiment, it was found that 4(or 5)-chloromethylglyoxaline hydrochloride readily condenses with ethyl sodiochloromalonate,

forming *ethyl 4(or 5)-glyoxalinemethylchloromalonate* (VII) in a yield amounting to 60 per cent. of the theoretical:



This ester is readily hydrolysed by boiling 20 per cent. hydrochloric acid, losing two molecules of ethyl alcohol and one of carbon dioxide, and thus becoming almost quantitatively converted into *r*- $\alpha$ -chloro- $\beta$ -glyoxaline-4(or 5)-propionic acid (VIII). This acid, when heated with concentrated aqueous ammonia at 110°, yields *r*- $\alpha$ -amino- $\beta$ -glyoxaline-4(or 5)-propionic acid (IX), that is, *r*-histidine, in a yield amounting to 38 per cent. of the theoretical:



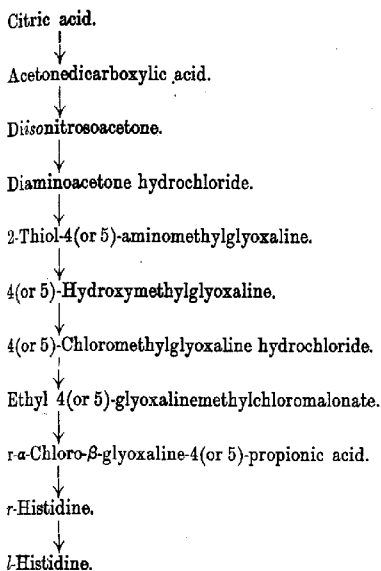
The identity of this synthetic *r*-histidine with that obtained by racemising the naturally occurring *l*-*avo*-variety (Fränkel, *Beitr. chem. Physiol. Path.*, 1906, **8**, 156; Ewins and Pyman, *this vol.*, p. 339) has been established by analyses of the base and two salts, and by the agreements in the melting points of the base and four salts from either source and the respective mixtures.

The synthesis of histidine itself, that is, the naturally occurring *l*-*avo*-modification, has been completed by the resolution of the racemic variety. When equimolecular amounts of *r*-histidine and *d*-tartaric acid were crystallised from water, there separated first *d*-histidine *d*-hydrogen tartrate (melting point 234° (corr.);  $[\alpha]_D + 13.3^\circ$ ). This salt is sparingly soluble in water, and is obtained in a yield amounting to about 90 per cent. of the theoretical. The hitherto unknown *d*-histidine was regenerated from it, and found to melt at 287—288° (corr.), and to have  $[\alpha]_D + 39.3^\circ$ . The mother liquors from the *d*-base-*d*-acid then deposited the easily soluble but magnificently crystalline *l*-histidine *d*-hydrogen tartrate (melting point 172—173° (corr.);  $[\alpha]_D + 17.4^\circ$ ) in a yield amounting to nearly 80 per cent. of the theoretical. The *l*-histidine regenerated from this was found to have  $[\alpha]_D - 36.6^\circ$ , and was therefore further purified by conversion into the sparingly soluble *l*-histidine *l*-hydrogen tartrate (melting point 234° (corr.);  $[\alpha]_D - 12.1^\circ$ ). After regeneration from this salt, *l*-histidine melted at 287—288° (corr.), and had  $[\alpha]_D - 38.1^\circ$ .

The specific rotatory power is thus substantially in agreement

with that found for natural histidine,  $[\alpha]_D -39.7^\circ$  by Kossel and Kutscher (*Zeitsch. physiol. Chem.*, 1899, **28**, 382).

The following scheme shows the steps by which the synthesis of histidine has been effected:



There are a few other points of interest about some of the compounds described. It has already been stated that ethyl 4(or 5)-glyoxalinemethylchloromalonate yields r- $\alpha$ -chloro- $\beta$ -glyoxaline-4(or 5)-propionic acid on hydrolysis with acid, and it was thought that this ester would give the corresponding tartronic acid (X) when boiled with alkali:

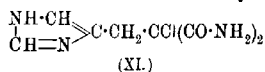


This, however, was not the case, boiling dilute aqueous sodium hydroxide eliminating one of the nitrogen atoms of the glyoxaline nucleus in the form of ammonia. This remarkable reaction has not yet been further studied, but one other case of a glyoxaline derivative behaving similarly is described in the literature. Thus, Pinner (*Ber.*, 1905, **38**, 2560) found that metapilocarpine—an isomeride of



pilocarpine obtained from the hydrochloride of the latter by prolonged heating at a high temperature—lost half its nitrogen as methylamine when boiled with aqueous potassium hydroxide, nitrogenous acids being produced at the same time. Normally, the glyoxaline ring is quite unaffected by boiling alkalis, except in the case of its quaternary salts, which lose both atoms of nitrogen as the corresponding alkylamines (compare Pinner and Schwarz, *Ber.*, 1902, **35**, 2446).

Ethyl 4(or 5)-glyoxalinemethylchloromalonate gave, with cold alcoholic ammonia, 4(or 5)-glyoxalinemethylchloromalonamide (XI), which was isolated in the form of its hydrochloride; strong

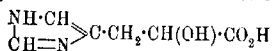


(XI.)

ammonia at 110°, however, gave an uninviting product, which was neglected.

It should be mentioned that the *r*- $\alpha$ -chloro- $\beta$ -glyoxaline-4(or 5)-propionic acid mentioned above melts at 201° (corr.), that is, 10° higher than the  $\alpha$ -chloro- $\beta$ -glyoxaline-4(or 5)-propionic acid described by Windaus and Vogt (*Beitr. chem. Physiol. Path.*, 1903, **11**, 406). The latter, however, was prepared from *l*-histidine, and is doubtless the corresponding optically active variety.

*r*- $\alpha$ -Hydroxy- $\beta$ -glyoxaline-4(or 5)-propionic acid (XII) has also been prepared by the action of hot moist silver oxide on *r*- $\alpha$ -chloro-

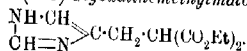


(XII.)

$\beta$ -glyoxaline-4(or 5)-propionic acid. It melts at 222° (corr.), thus differing from the "oxydeaminohistidine," that is,  $\alpha$ -hydroxy- $\beta$ -glyoxaline-4(or 5)-propionic acid, melting at 204°, prepared by Fränkel (*Monatsh.*, 1903, **24**, 229) by the action of silver nitrite on *l*-histidine. Here again the difference lies, no doubt, in the optical activity of the acid obtained from the natural product. Both acids crystallise with one molecule of water of crystallisation.

#### EXPERIMENTAL.

Ethyl 4(or 5)-Glyoxalinemethylmalonate,



Twenty grams of 4(or 5)-chloromethylglyoxaline hydrochloride were brought into reaction with two molecular proportions of ethyl sodiomalonate, and the product worked up in the same way as that from ethyl sodiochloromalonate (p. 1392); the yield was 21 grams

of *ethyl 4(or 5)-glyoxalinemethylmalonate hydrogen oxalate*, that is, 49 per cent. of the theoretical.

*Ethyl 4(or 5)-glyoxalinemethylmalonate hydrogen oxalate* crystallises from water in large, hard, clear, nearly rectangular, oblong plates, which melt at 155–158° (corr.). It is anhydrous, sparingly soluble in cold, but readily so in hot, water:

0.1488 gave 0.2564 CO<sub>2</sub> and 0.0727 H<sub>2</sub>O. C=47.0; H=5.5.

0.1413 „ 10.6 c.c. N<sub>2</sub> at 19° and 778 mm. N=9.0.

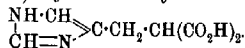
C<sub>11</sub>H<sub>16</sub>O<sub>4</sub>N<sub>2</sub>·C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> requires C=47.2; H=5.5; N=8.5 per cent.

The base was regenerated from the oxalate by means of sodium carbonate and ether; after distillation of the solvent, it remained as a yellow oil, which became very viscid when cold, but readily poured when warm. It showed no signs of crystallisation after long keeping. It is sparingly soluble in water, but readily so in alcohol or ether.

The *hydrochloride* occurs as a deliquescent mass of needles, melting indefinitely at 50–70°, and readily soluble in water, alcohol, acetone, or ethyl acetate.

The *hydriodide* is a crystalline salt of similar properties.

4(or 5)-Glyoxalinemethylmalonic Acid,



*Ethyl 4(or 5)-glyoxalinemethylmalonate* was boiled with an excess of baryta water for several hours; a stream of carbon dioxide was then led through the liquid, and the barium carbonate removed by filtration. The clear filtrate, containing the barium salts of 4(or 5)-glyoxalinemethylmalonic acid and  $\beta$ -glyoxaline-4(or 5)-propionic acid, was then made up to a known volume, and the barium in an aliquot portion determined.

The liquor was then treated with a quantity of oxalic acid exactly sufficient to remove the barium, filtered from barium oxalate, and concentrated to low bulk, when 4(or 5)-glyoxalinemethylmalonic acid crystallised out on cooling; the mother liquor contained  $\beta$ -glyoxaline-4(or 5)-propionic acid.

4(or 5)-Glyoxalinemethylmalonic acid crystallises from water in beautiful, clear, hexagonal plates. It is easily soluble in hot water, but sparingly so in cold water or alcohol:

0.1512 gave 0.2530 CO<sub>2</sub> and 0.0596 H<sub>2</sub>O. C=45.6; H=4.4.

C<sub>7</sub>H<sub>8</sub>O<sub>4</sub>N<sub>2</sub> requires C=45.6; H=4.4 per cent.

When heated, this malonic acid melts and effervesces at 180° (corr.), losing carbon dioxide; it resolidifies while still hot, and does not then melt until 207° (corr.),  $\beta$ -glyoxaline-4(or 5)-propionic acid,

$C_3H_3N_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$ , being formed. A quantity of the latter acid was prepared in this manner, and after recrystallisation from water melted at  $209-210^\circ$  (corr.). (Found,  $C=51.1$ ;  $H=6.0$ . Calc.,  $C=51.4$ ;  $H=5.8$  per cent.) Knoop and Windaus, who have previously prepared this acid in other ways (*Beitr. chem. Physiol. Path.*, 1905, 7, 144), give m. p.  $208-209^\circ$ .

*Ethyl 4(or 5)-Glyoxalinemethylacetoacetate,*  
 $C_3H_3N_2 \cdot CH_2 \cdot CH(COMe) \cdot CO_2Et.$

This compound was prepared by condensing 4(or 5)-chloromethylglyoxaline hydrochloride (1 mol.) with ethyl sodioacetoacetate (2 mols.).

The *hydrogen oxalate* crystallises from water in rosettes of thin, clear plates, which melt and decompose at  $145-146^\circ$  (corr.). It is anhydrous, fairly readily soluble in cold water, and easily so in hot:

0.1535 gave 0.2704  $CO_2$  and 0.0751  $H_2O$ .  $C=48.0$ ;  $H=5.5$ .

0.1148 „ 9.3 c.c.  $N_2$  at  $17^\circ$  and 754 mm.  $N=9.5$ .

$C_{10}H_{11}O_3N_2 \cdot C_2H_2O_4$  requires  $C=48.0$ ;  $H=5.3$ ;  $N=9.3$  per cent.

*Ethyl 4(or 5)-Glyoxalinemethylmethacetoacetate,*  
 $C_3H_3N_2 \cdot CH_2 \cdot CMe(COMe) \cdot CO_2Et.$

This compound was prepared by condensing 4(or 5)-chloromethylglyoxaline hydrochloride (1 mol.) with ethyl sodiomethacetoacetate (2 mols.).

The *hydrogen oxalate* crystallises from water in clusters of beautiful, clear, glistening plates, which melt and decompose at  $155-156^\circ$  (corr.). It is anhydrous, fairly readily soluble in cold water, and easily so in hot:

0.1525 gave 0.2874  $CO_2$  and 0.0823  $H_2O$ .  $C=51.4$ ;  $H=6.1$ .

0.1300 „ 10.2 c.c.  $N_2$  at  $18^\circ$  and 762 mm.  $N=9.2$ .

$(C_{11}H_{16}O_3N_2)_4 \cdot (C_2H_2O_4)_3$  requires  $C=51.4$ ;  $H=6.1$ ;  $N=9.6$  per cent.

On regenerating the base, dissolving it in absolute alcoholic hydrogen chloride, and evaporating nearly to dryness in an evacuated desiccator, a crystalline *hydrochloride* separated in deliquescent needles, which were very easily soluble in water, alcohol, acetone, or ethyl acetate.

*Ethyl 4(or 5)-Glyoxalinemethylchloromalonate,*  

$$\begin{array}{c} NH \cdot CH \\ CH=N \end{array} > C \cdot CH_2 \cdot CCl(CO_2Et)_2.$$

To 9.2 grams of sodium, dissolved in 200 c.c. of absolute alcohol, 78 grams of ethyl chloromalonate were added, followed by a solution

of 30.6 grams of 4(or 5)-chloromethylglyoxaline hydrochloride in 150 c.c. of absolute alcohol, the liquid being kept cold during both additions. The mixture was then boiled for one and a-half hours under a reflux condenser, filtered from sodium chloride, and the solvent removed by distillation. The resulting oil was mixed with dilute hydrochloric acid, and extracted with ether to remove the non-basic esters; the liquor was then rendered alkaline with sodium carbonate, and completely extracted with ether. The residue, after evaporation of the solvent, consisting of a clear, brown oil, was dissolved in a solution of 25 grams of oxalic acid in 550 c.c. of boiling water, and decolorised with animal charcoal. On cooling, 39 grams of pure *ethyl 4(or 5)-glyoxalinemethyl chloromalonate hydrogen oxalate* separated, and further small quantities (about 3 grams) were obtained from the mother liquors, the yield thus amounting to 60 per cent. of the theoretical.

*Ethyl 4(or 5)-glyoxalinemethylchloromalonate hydrogen oxalate* crystallises from water in shimmering leaflets, which melt and decompose at 176° (corr.). This salt is sparingly soluble in cold water, but readily so in hot. It is anhydrous:

0.1517 gave 0.2442 CO<sub>2</sub> and 0.0647 H<sub>2</sub>O. C=43.9; H=4.8.

0.1507 „ 0.2415 CO<sub>2</sub> „ 0.0635 H<sub>2</sub>O. C=43.7; H=4.7.

0.2315 „ 0.0991 AgCl. Cl=10.6.

(C<sub>11</sub>H<sub>15</sub>O<sub>4</sub>N<sub>2</sub>Cl)<sub>10</sub>.(C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>)<sub>3</sub> requires C=43.8; H=4.8;  
Cl=10.4 per cent.

The *hydrochloride* crystallises from acetone in beautiful, large, glistening, diamond-shaped plates, which melt at 148–149° (corr.). It is anhydrous, readily soluble in water or alcohol, fairly readily so in hot acetone, and sparingly so in cold acetone:

0.1556 gave 0.2423 CO<sub>2</sub> and 0.0739 H<sub>2</sub>O. C=42.5; H=5.3.

C<sub>11</sub>H<sub>15</sub>O<sub>4</sub>N<sub>2</sub>Cl.HCl requires C=42.4; H=5.2 per cent.

Aqueous solutions of the hydrochloride give a sparingly soluble precipitate with picric acid or Meyer's solution, and give a deep red coloration with sodium diazobenzene-*p*-sulphonate in alkaline solution. The free base was regenerated by shaking the salts with sodium carbonate and ether; it formed a viscid oil which did not crystallise, and is easily soluble in alcohol, ether, or chloroform; but very sparingly so in water.

*Ethyl 4(or 5)-glyoxalinemethylchloromalonate* yields, on hydrolysis with 20 per cent. hydrochloric acid, *r*- $\alpha$ -chloro- $\beta$ -glyoxaline-4(or 5)-propionic acid. When hydrolysed by boiling with dilute aqueous sodium hydroxide, however, it loses half its nitrogen as ammonia. This was determined quantitatively by absorption in dilute sulphuric acid in the usual way.

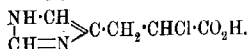
0.2532 (oxalate) gave  $\text{NH}_3$  requiring 7.4 c.c.  $N/10\text{-H}_2\text{SO}_4$ ;  
 $N=4.1$ .

0.5008 (oxalate) gave  $\text{NH}_3$  requiring 15.2 c.c.  $N/10\text{-H}_2\text{SO}_4$ ;  
 $N=4.3$ .

$(\text{C}_{11}\text{H}_{15}\text{O}_4\text{N}_2\text{Cl})_4 \cdot (\text{C}_2\text{H}_2\text{O}_4)_3$  requires total  $N=8.2$  per cent.

With cold ammonia, it yields 4(or 5)-glyoxalinemethylchloromalonamide, but with strong ammonia at  $110^\circ$  only dark brown, uninviting products are obtained.

*r-α-Chloro-β-glyoxaline-4(or 5)-propionic Acid,*



Ten grams of ethyl 4(or 5)-glyoxalinemethylchloromalonate hydrochloride were boiled with 100 c.c. of 20 per cent. hydrochloric acid for forty-five minutes. The liquor was evaporated to dryness under diminished pressure, moistened with water, and again evaporated to dryness. The resulting colourless varnish was dissolved in 300 c.c. of cold water, digested cold with the silver carbonate from 8 grams of silver nitrate, filtered from silver chloride, and treated with hydrogen sulphide. After the removal of silver sulphide, the filtrate was evaporated to low bulk under diminished pressure, and allowed to crystallise, when 5.1 grams of pure *r-α-chloro-β-glyoxaline-4(or 5)-propionic acid* were obtained; this yield represents 91 per cent. of the theoretical.

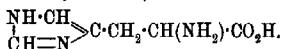
*r-α-Chloro-β-glyoxaline-4(or 5)-propionic acid* crystallises from water in white, star-like clusters of prismatic needles. It is anhydrous, and melts and decomposes at  $201^\circ$  (corr.); but the melting point varies considerably with the rate of heating, and may be found anywhere between  $198^\circ$  and  $204^\circ$  (corr.). It is sparingly soluble in cold water, alcohol, or acetone, but readily so in hot water:

0.1547 gave 0.2334  $\text{CO}_2$  and 0.0571  $\text{H}_2\text{O}$ .  $C=41.1$ ;  $H=4.1$ .

0.1604 „ 0.1319  $\text{AgCl}$ .  $\text{Cl}=20.3$ .

$\text{C}_6\text{H}_7\text{O}_2\text{N}_2\text{Cl}$  requires  $C=41.3$ ;  $H=4.1$ ;  $\text{Cl}=20.3$  per cent.

The *α-chloro-β-glyoxaline-4(or 5)-propionic acid* previously described by Windaus and Vogt (*Beitr. chem. Physiol. Path.*, 1908, 11, 406) is stated to melt at  $191^\circ$ ; it is doubtlessly the optically active variety corresponding with *L*-histidine, from which it was prepared.

*Synthesis of r-Histidine.*

Two and a-half grams of *r*- $\alpha$ -chloro- $\beta$ -glyoxaline-4 (or 5)-propionic acid were dissolved in 50 c.c. of concentrated ammonia (D 0.880), and heated at 110° under pressure for three hours. The liquor was then evaporated to dryness under diminished pressure, and the residue dissolved in a little water and again evaporated. The residue was dissolved in a few c.c. of water, and set aside, when 1.1 grams of *r*-histidine monohydrochloride separated in stout needles, melting at 110—115°; after recrystallisation from water, this salt melted at 117—119° (corr.), after sintering earlier.

A larger quantity of synthetic *r*-histidine was then prepared as follows: Twenty grams of ethyl 4 (or 5)-glyoxalinemethylchloromalonate were converted into *r*- $\alpha$ -chloro- $\beta$ -glyoxaline-4 (or 5)-propionic acid hydrochloride by boiling for half an hour with 200 c.c. of 20 per cent. hydrochloric acid, and evaporating the liquor to dryness under diminished pressure.

The resulting colourless varnish was again twice dissolved in water, and evaporated to dryness to remove free hydrochloric acid. It was then dissolved in 240 c.c. of concentrated ammonia (D 0.880), and heated under pressure to 110° for three hours. The liquor was then evaporated to dryness under diminished pressure to remove the excess of ammonia, and the residue dissolved in about 40 c.c. of water. On keeping overnight in an evacuated desiccator over sulphuric acid, the liquor was covered with a crust of ammonium chloride. After the removal of this by filtration, the filtrate began to deposit crystals, and on keeping became semi-solid. The crystals were collected after about half an hour, and, after recrystallisation from water, melted at 117—119° (corr.); they were *r*-histidine monohydrochloride. On concentrating the mother liquors, further crops of this salt and ammonium chloride were obtained; these were separated by fractional crystallisation from water, and a total quantity of 6.3 grams of *r*-histidine monohydrochloride was isolated in a pure state; this yield is 38 per cent. of the theoretical.

*Synthetic r-Histidine.*

*r*-Histidine monohydrochloride forms clusters of stout needles (from water), which sinter at 112°, and melt at 117—119° (corr.). It contains two molecules of water of crystallisation, of which only about 1½ molecules are lost at 100°. This salt is easily soluble in water, but sparingly so in alcohol:

0.1556 \* lost 0.0196 at 100°.  $\text{H}_2\text{O}=12.6$ .

0.1530 \* gave 0.1781  $\text{CO}_2$  and 0.0857  $\text{H}_2\text{O}$ .  $\text{C}=31.7$ ;  $\text{H}=6.3$ .

0.1009 \* „ 16.0 c.c.  $\text{N}_2$  at 16° and 765 mm.  $\text{N}=18.9$ .

0.1634 \* „ 0.1010  $\text{AgCl}$ .  $\text{Cl}=15.3$ .

$\text{C}_6\text{H}_9\text{O}_2\text{N}_3 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$  requires  $\text{C}=31.6$ ;  $\text{H}=6.2$ ;  $\text{N}=18.5$ ;

$\text{Cl}=15.6$ ; and  $1\frac{1}{2}\text{H}_2\text{O}=11.9$  per cent.

When this salt was dissolved in a little water, and a large excess of absolute alcoholic hydrogen chloride added, the dihydrochloride was precipitated in an amorphous form, but quickly became a crystalline powder on stirring. This salt began to sinter at 230°, and decomposed at 235—236° (corr.):

0.1505 gave 0.1750  $\text{CO}_2$  and 0.0638  $\text{H}_2\text{O}$ .  $\text{C}=31.7$ ;  $\text{H}=4.8$ .

0.1088 „ 0.1359  $\text{AgCl}$ .  $\text{Cl}=30.9$ .

$\text{C}_6\text{H}_9\text{O}_2\text{N}_3 \cdot 2\text{HCl}$  requires  $\text{C}=31.6$ ;  $\text{H}=4.9$ ;  $\text{Cl}=31.1$  per cent.

On dissolving the dihydrochloride in a little water and adding alcohol, the sesquihydrochloride separated on keeping in clusters of prismatic needles, which melted at 168—170° (corr.).

These three hydrochlorides of synthetic *r*-histidine were compared with the corresponding salts of *r*-histidine prepared by racemising *l*-histidine, and found to be identical with them; in each case the corresponding salt and the mixture of the synthetic and racemised salt melted simultaneously.

The melting point of racemised histidine dihydrochloride, given by Fränkel (*loc. cit.*) as 220°, and by Ewins and Pyman (*loc. cit.*) as 225° (corr.), is too low; a re-determination has shown that it should be 235—236° (corr.).

*r*-Histidine was prepared from the synthetic monohydrochloride by digesting it with silver oxide, and filtering to remove silver chloride, removing the excess of silver with hydrogen sulphide, and evaporating to low bulk under diminished pressure. After recrystallisation from water, it formed well defined quadrilateral plates, which decomposed at 283° (corr.) simultaneously with a specimen prepared by racemising *l*-histidine, and a mixture of the two in the same bath. It is anhydrous, and is sparingly soluble in cold water, easily so in hot water, but almost insoluble in absolute alcohol and the other usual organic solvents:

0.1514 gave 0.2551  $\text{CO}_2$  and 0.0806  $\text{H}_2\text{O}$ .  $\text{C}=46.0$ ;  $\text{H}=6.0$ .

0.0859 „ 20.0 c.c.  $\text{N}_2$  at 22° and 763 mm.  $\text{N}=27.0$ .

$\text{C}_6\text{H}_9\text{O}_2\text{N}_3$  requires  $\text{C}=46.4$ ;  $\text{H}=5.9$ ;  $\text{N}=27.1$  per cent.

*r*-Histidine dipicrate was also prepared from the synthetic monohydrochloride, and proved to be identical with the salt described by Ewins and Pyman (*loc. cit.*). It should be mentioned that this

\* Air-dried.

salt—from either source—when dried in the air for only a short time, melts at about  $103^{\circ}$  (corr.), and then, after drying at  $100^{\circ}$ , sometimes melts between  $140^{\circ}$  and  $150^{\circ}$ , although it does not decompose until  $190^{\circ}$ . When thoroughly air-dried, however, and then dried at  $100^{\circ}$ , it sinters at about  $183^{\circ}$ , and melts and decomposes at  $190^{\circ}$  (corr.).

*Resolution of r-Histidine.*

With the object of finding a suitable method for the resolution of synthetic *r*-histidine, some salts of natural histidine with optically active acids were first prepared.

The histidine used for this purpose was prepared from hæmoglobin, and the free base was obtained from its hydrochloride by means of silver carbonate, a method due to Fränkel (*Monatsh.*, 1903, **24**, 229). The base decomposed at  $287^{\circ}$  (corr.), a temperature considerably higher than that given by Fränkel, namely  $253^{\circ}$ , and it was therefore analysed. (Found, C=46.0; H=6.1. Calc., C=46.4; H=5.9 per cent.)

Its specific rotatory power was then determined in a 1-dm. tube: 0.2, in 10 c.c. of water at  $26^{\circ}$ , gave  $\alpha_D -0.74^{\circ}$ , whence  $[\alpha]_D -37.0^{\circ}$ . 1.015, in 25 c.c. of water at  $28^{\circ}$ , gave  $\alpha_D -1.49^{\circ}$ , whence  $[\alpha]_D -36.7^{\circ}$ .

Kossel and Kutscher (*Zeitsch. physiol. Chem.*, 1899, **28**, 382) give  $[\alpha]_D -39.7^{\circ}$ .

It was found that the *d*-camphorsulphonate and neutral *d*-tartrate of this base were very readily soluble in water, and crystallised from this solvent with difficulty.

*l*-Histidine *d*-hydrogen tartrate, however, crystallises from water in beautiful, large, clear, colourless, well defined prisms, often separating in triangular plates with bevelled edges. It is anhydrous, and easily soluble in water. This salt decomposes at  $172-173^{\circ}$  (corr.):

0.1535 gave 0.2188  $\text{CO}_2$  and 0.0718  $\text{H}_2\text{O}$ . C=38.9; H=5.2.

$\text{C}_6\text{H}_9\text{O}_2\text{N}_3\text{C}_4\text{H}_6\text{O}_6$  requires C=39.3; H=5.0 per cent.

The specific rotatory power of this salt was determined in a 2-dm. tube; it appears to diminish with increasing concentration:

0.1616, in 15 c.c. of water at  $24^{\circ}$ , gave  $\alpha_D +0.37^{\circ}$ , whence  $[\alpha]_D +17.2$ .

0.5587, in 15 c.c. of water at  $24^{\circ}$ , gave  $\alpha_D +1.26^{\circ}$ , whence  $[\alpha]_D +16.9$ .

0.7474, in 15 c.c. of water at  $25^{\circ}$ , gave  $\alpha_D +1.62^{\circ}$ , whence  $[\alpha]_D +16.3$ .

The base was then regenerated from the pure salt as follows, the



method adopted being substantially that used by Fränkel (*loc. cit.*) for the isolation of histidine from the hydrolytic products of hæmoglobin. The tartrate was dissolved in a large volume of water, and precipitated by mercuric chloride and sodium carbonate; the precipitate was thoroughly washed with water, dissolved in dilute hydrochloric acid, and treated with hydrogen sulphide. After the removal of mercuric sulphide, the liquor was evaporated to dryness under diminished pressure, moistened with water, and again evaporated to dryness to remove free hydrochloric acid. The residue was then dissolved in water, shaken with silver carbonate, filtered from silver chloride, treated with hydrogen sulphide, filtered from silver sulphide, and evaporated to low bulk, when the base crystallised out.

Its specific rotatory power was determined in a 2-dm. tube:

0.504, in 15 c.c. of water at 22°, gave  $\alpha_D -2.53^\circ$ , whence  $[\alpha]_D -37.7^\circ$ .

In view of the satisfactory crystalline nature of *l*-histidine *d*-hydrogen tartrate, it was determined to attempt the resolution of synthetic *r*-histidine by fractional crystallisation of the *d*-hydrogen tartrate, and 0.73 gram of synthetic *r*-histidine and 0.7 gram of *d*-tartaric acid were accordingly dissolved in a little water and kept. After a short time there crystallised out 0.6 gram of a sparingly soluble salt, melting at 234° (corr.), which is subsequently shown to be *d*-histidine *d*-hydrogen tartrate, and the mother liquors from this salt, after spontaneous evaporation in a desiccator over sulphuric acid, deposited about 0.2 gram of clear prisms, melting at 172–173° (corr.), which were identical with *l*-histidine *d*-hydrogen tartrate. The resolution of a larger quantity of synthetic histidine was then carried out as follows: 3.5 grams of synthetic *r*-histidine and 3.4 grams of *d*-tartaric acid were dissolved in water, and evaporated to a volume of about 20 c.c., when crystals began to separate from the hot solution. The evaporation was then continued to a volume of about 15 c.c., and the liquor set aside. Clusters of prisms, melting at 234° (corr.), and amounting to 2.9 grams, were then collected, and on concentrating the mother liquor and keeping, a further 0.28 gram of the same salt were obtained.

On recrystallising this salt from water, 3.05 grams of *d*-histidine *d*-hydrogen tartrate were obtained.

*d*-Histidine *d*-hydrogen tartrate crystallises from water in clusters of small prisms, which decompose at 234° (corr.). It dissolves in 25 to 30 parts of cold water, and more readily in hot water. It is anhydrous:

0.1561 gave 0.2237  $\text{CO}_2$  and 0.0694  $\text{H}_2\text{O}$ .  $\text{C}=39.1$ ;  $\text{H}=5.0$ .

$\text{C}_6\text{H}_9\text{O}_2\text{N}_3, \text{C}_4\text{H}_6\text{O}_6$  requires  $\text{C}=39.3$ ;  $\text{H}=5.0$  per cent.

Its specific rotatory power was determined in a 2-dcm. tube:

0.9220, in 25 c.c. of water at  $28^\circ$ , gave  $\alpha_D + 0.98^\circ$ , whence  $[\alpha]_D + 13.3^\circ$ .

This salt was converted into the free base by the method given above.

*d-Histidine* crystallises from water in beautiful, colourless, monoclinic plates, forming elongated hexagons. It decomposes at  $287\text{--}288^\circ$  (corr.), and is anhydrous. It is sparingly soluble in cold water, easily so in hot water, and almost insoluble in absolute alcohol and the other usual organic solvents:

0.1532 gave 0.2608  $\text{CO}_2$  and 0.0807  $\text{H}_2\text{O}$ .  $\text{C}=46.4$ ;  $\text{H}=5.9$ .

$\text{C}_6\text{H}_9\text{O}_2\text{N}_3$  requires  $\text{C}=46.4$ ;  $\text{H}=5.9$  per cent.

Its specific rotatory power was determined in a 2-dcm. tube:

0.401, in 15 c.c. of water at  $23^\circ$ , gave  $\alpha_D + 2.10^\circ$ , whence  $[\alpha]_D + 39.3^\circ$ .

The mother liquor from the *d*-histidine *d*-hydrogen tartrate was then somewhat concentrated, and inoculated with a trace of the *l*-histidine *d*-hydrogen tartrate obtained in the preliminary experiment mentioned above, when there crystallised 1.65 grams of this salt in clear prisms, decomposing at  $172\text{--}173^\circ$  (corr.), and on concentrating the mother liquors, a further 1.05 grams, equally pure. The ultimate mother liquors which continued to deposit crystalline material were neglected.

The melting point of the *l*-base-*d*-acid was unchanged by recrystallising the salt, or mixing it with natural *l*-histidine *d*-hydrogen tartrate. The salt was, however, recrystallised, and its specific rotatory power was determined in a 2-dcm. tube, and found to be in agreement with that of the natural salt at corresponding concentrations:

0.8625, in 25 c.c. of water at  $27^\circ$ , gave  $\alpha_D + 1.20^\circ$ , whence  $[\alpha]_D + 17.4^\circ$ .

0.8200, in 15 c.c. of water at  $23^\circ$ , gave  $\alpha_D + 1.76^\circ$ , whence  $[\alpha]_D + 16.1^\circ$ .

The recrystallised salt and its mother liquor (=2.7 grams of *l*-base-*d*-acid) were then recombined, and the base regenerated.

The specific rotatory power of the latter was determined in a 2-dcm. tube:

0.4143, in 15 c.c. of water at  $26^\circ$ , gave  $\alpha_D - 2.02^\circ$ , whence  $[\alpha]_D - 36.6^\circ$ .

This figure being somewhat low, the whole of the regenerated

base (1.1 grams) was converted into the *l*-hydrogen tartrate, and crystallised from water.

*l*-Histidine *l*-hydrogen tartrate crystallises from water in clusters of prisms, which decompose at 234° (corr.). It is sparingly soluble in cold water. A specimen of this salt prepared from natural histidine had the same melting point and specific rotatory power. The latter was determined in a 2-dcm. tube:

0.6792 (synthetic), in 15 c.c. of water at 22°, gave  $\alpha_D - 1.10^\circ$ ,  
whence  $[\alpha]_D - 12.1^\circ$ .

0.6796 (natural), in 15 c.c. of water at 25°, gave  $\alpha_D - 1.10^\circ$ ,  
whence  $[\alpha]_D - 12.1^\circ$ .

The synthetic salt was then converted into the free base in the usual way.

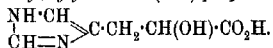
Synthetic *l*-histidine crystallised from water in monoclinic plates, forming elongated hexagons, which decomposed at 287–288° (corr.). Its decomposition point is not depressed by admixture of the base with natural *l*-histidine, but this is of little importance, since it is only depressed about 2° by admixture with *r*-histidine. It is sparingly soluble in cold water, easily so in hot water, and almost insoluble in absolute alcohol and the other usual organic solvents:

0.1402 gave 0.2358 CO<sub>2</sub> and 0.0756 H<sub>2</sub>O. C=45.9; H=6.0.  
C<sub>6</sub>H<sub>9</sub>O<sub>2</sub>N<sub>3</sub> requires C=46.4; H=5.9 per cent.

Its specific rotatory power was determined in a 2-dcm. tube:

0.3447, in 15 c.c. of water at 26°, gave  $\alpha_D - 1.75^\circ$ , whence  
 $[\alpha]_D - 38.1^\circ$ .

*r*- $\alpha$ -Hydroxy- $\beta$ -glyoxaline-4(or 5)-propionic Acid,



This acid results from the action of silver hydroxide on a hot aqueous solution of *r*- $\alpha$ -chloro- $\beta$ -glyoxaline-4(or 5)-propionic acid. After the removal of silver chloride, the solution is treated with hydrogen sulphide, filtered from silver sulphide, and concentrated, when the hydroxy-acid crystallises out.

*r*- $\alpha$ -Hydroxy- $\beta$ -glyoxaline-4(or 5)-propionic acid crystallises from water in prisms, which, after drying at 100°, melt at 222° (corr.). It contains one molecule of water of crystallisation, which is not lost at 100°, and is sparingly soluble in cold water or alcohol, but readily so in hot water:

0.1516 \* gave 0.2290 CO<sub>2</sub> and 0.0776 H<sub>2</sub>O. C=41.2; H=5.7.

0.1007 „ 14.0 c.c. N<sub>2</sub> at 16° and 755 mm. N=16.3.

C<sub>6</sub>H<sub>8</sub>O<sub>3</sub>N<sub>2</sub>·H<sub>2</sub>O requires C=41.4; H=5.8; N=16.1 per cent.

Oxydeaminohistidine, the  $\alpha$ -hydroxy- $\beta$ -glyoxaline-4(or 5)-propionic acid obtained by the action of silver nitrite on *l*-histidine hydrochloride, also crystallises with 1H<sub>2</sub>O. It melts at 204° (Fränkel, *Monatsh.*, 1903, **24**, 229), and is, of course, the optically active variety corresponding with *l*-histidine.

4(or 5)-Glyoxalinemethylchloromalonamide,  
C<sub>3</sub>H<sub>8</sub>N<sub>2</sub>·CH<sub>2</sub>·CCl(CO·NH<sub>2</sub>)<sub>2</sub>.

One gram of ethyl 4(or 5)-glyoxalinemethylchloromalonate hydrochloride was dissolved in a mixture of 20 c.c. of concentrated ammonia and 10 c.c. of alcohol, and the clear solution kept overnight. It was then evaporated to dryness under diminished pressure, the residue extracted with absolute alcohol, and filtered to remove ammonium chloride, these operations being repeated two or three times. The final alcoholic residue occurred as a varnish, which gave, with absolute alcoholic hydrogen chloride, 0.7 gram of 4(or 5)-glyoxalinemethylchloromalonamide hydrochloride as a crystalline precipitate. This salt was dissolved in a little water and mixed with absolute alcoholic hydrogen chloride, and on keeping separated in very pale buff, long, clear spikes, which darkened at 240° and decomposed at 245° (corr.).

It is anhydrous, readily soluble in water, but sparingly so in alcohol:

0.1500 gave 0.1821 CO<sub>2</sub> and 0.0567 H<sub>2</sub>O. C=33.1; H=4.2.

0.0805 „ 14.8 c.c. N<sub>2</sub> at 18° and 766 mm. N=21.7.

0.1858 „ 0.2100 AgCl. Cl=27.9.

C<sub>7</sub>H<sub>8</sub>O<sub>2</sub>N<sub>4</sub>Cl·HCl requires C=33.2; H=4.0; N=22.1;

Cl=28.0 per cent.

THE WELLCOME CHEMICAL WORKS,  
DARTFORD, KENT.

\* Dried at 100°.

CLVIII.—*The Interaction of Metallic Oxides and Phosphoryl Chloride, Alone and in the Presence of Certain Organic Compounds.*

By HENRY BASSETT, jun., and HUGH STOTT TAYLOR.

APATITE,  $(\text{Ca}_3\text{P}_2\text{O}_8)_3$ ,  $\text{CaF}_2$ , and wagnerite,  $\text{Mg}_3\text{P}_2\text{O}_8 \cdot \text{MgF}_2$ , are two important minerals, the formulæ of which are usually written as indicated, suggesting that the compounds are to be regarded as complex derivatives of the metallic fluoride (or, in some cases, chloride), in which the halogen is directly attached to the metal.

There is, however, little experimental foundation for such an assumption, and in some ways it is perhaps more probable that the halogen is more closely associated with the phosphorus.

The following investigation was commenced in the hope that by preparing simple chlorophosphates and determining their constitution, it would be possible to throw light on the nature of more complex halogen compounds such as the above.

We found that when freshly ignited lime and freshly distilled phosphoryl chloride were mixed and allowed to remain at the ordinary temperature or gently boiled, a well crystallised compound was gradually formed, which analysis showed to have the formula  $\text{CaO} \cdot 2\text{POCl}_3$ .

This behaviour is not restricted to lime, and magnesia gives either  $\text{MgO} \cdot 2\text{POCl}_3$  or  $\text{MgO} \cdot 3\text{POCl}_3$ , according to the conditions of the experiment. We have also obtained well crystallised compounds,  $\text{MnO} \cdot 3\text{POCl}_3$  and  $\text{ZnO} \cdot 3\text{POCl}_3$ , but not in an absolutely pure state, owing to various difficulties which will be referred to shortly. Lime also yields a compound with three molecules of phosphoryl chloride in certain circumstances.

All the other metallic oxides which we have investigated ( $\text{CdO}$ ,  $\text{CoO}$ ,  $\text{CuO}$ ,  $\text{Cu}_2\text{O}$ ,  $\text{HgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ) react with phosphoryl chloride, but apparently not in such a simple manner as do lime and magnesia, and the chloride of the metal appears to be the chief product.

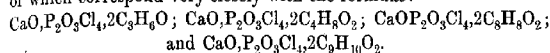
As was to be expected, these compounds of phosphoryl chloride are extremely sensitive to moisture, and in consequence of this the analyses often show low values for the chlorine, and a deficit, sometimes of several per cent., which it is almost impossible to prevent entirely.

In such cases, if the deficit is taken to be due to the replacement of a certain amount of chlorine by hydroxyl, it is found that the

atomic ratio of the total chlorine to phosphorus is almost exactly as three to one, as it should be, of course, for a compound of phosphoryl chloride.

Having found that phosphoryl chloride and certain oxides readily combined to give the compounds above mentioned, the effect of solvents on the course of the reaction was investigated.

It was found that when lime was added to a solution of phosphoryl chloride in acetone, ethyl acetate, methyl benzoate, or ethyl benzoate, which had been dried over calcium chloride and redistilled, a vigorous reaction occurred, which in the first two cases was sufficient to cause the solvent to boil. Some hydrogen chloride is evolved during this process, and the lime passes into solution. The solution on cooling deposits beautiful prismatic crystals, the analyses of which correspond very closely with the formulae:



These compounds are clearly the compound  $\text{CaO}, \text{P}_2\text{O}_5\text{Cl}_4$  crystallised with two molecules of ketone or ester. In agreement with this view is the fact that the organic part of the molecule can be changed by simple recrystallisation from another solvent. Thus by recrystallising the ethyl acetate compound from acetone, the acetone compound is obtained and vice versa.

Exactly similar organic derivatives have been obtained, using magnesium oxide and manganous oxide.

The formation of these organic compounds is brought about by traces of moisture present in the organic solvents, or which are absorbed during the course of the experiment, and there is some reason for thinking that the moisture acts preferably on the previously formed compound  $\text{CaO}, 2\text{POCl}_3$ , rather than on the phosphoryl chloride. In any case, the organic compounds can be obtained equally well by treating the previously prepared compound  $\text{CaO}, 2\text{POCl}_3$  with the organic solvent in which it dissolves, yielding a solution from which the organic derivative of the compound  $\text{CaO}, \text{P}_2\text{O}_5\text{Cl}_4$  crystallises.

The compounds of pyrophosphoryl chloride,  $\text{P}_2\text{O}_5\text{Cl}_4$ , obtained by us seem of especial interest as confirming the results obtained by Besson (*Compt. rend.*, 1897, **124**, 1099), who showed that this compound is the first product of the action of moisture on phosphoryl chloride which can be isolated. He was, however, never able to obtain more than a very small amount of pyrophosphoryl chloride in this way. It is therefore of interest to obtain derivatives of this compound which indicate quantitative conversion of phosphoryl chloride into pyrophosphoryl chloride, derivatives, moreover, which are well crystallised and well defined. On solution of these

in water, orthophosphoric acid is formed immediately, and this is in agreement with the behaviour of pyrophosphoryl chloride itself, as stated by Geuther and Michaelis (*Ber.*, 1871, **4**, 766).

No compounds of phosphoryl chloride with oxides have been obtained by previous workers, and from what has been said it will be seen that the statement found sometimes (Dammer "*Handbuch*," 1894, II, **1**, 134; Casselmann, *Annalen*, 1856, **98**, 228) that phosphoryl chloride reacts with metallic oxides to form chloride and phosphate of the metal requires qualifying. Gustavson (*J. Russ. Phys. Chem. Soc.*, 1871, **3**, 225) showed that boron trioxide and phosphoryl chloride react with formation of a double compound,  $\text{BCl}_3 \cdot \text{POCl}_3$ .

The oxidic compounds described in the present paper seem of especial interest from the fact that any salt-like character is only very feebly developed, their behaviour being more typical of that of "molecular compounds." This is unusual in the case of metallic oxides which usually give rise to salts. We consider, however, that there is no fundamental structural difference between, for example,  $\text{CaO} \cdot 2\text{POCl}_3$  and  $\text{CaO} \cdot 2\text{PO}(\text{OH})_3$  [ $\text{CaH}_4\text{P}_2\text{O}_8 \cdot \text{H}_2\text{O}$ ], and that from some points of view the first compound may be regarded as derived from the second by replacement of the hydroxyl groups by chlorine. It seems to us also that the existence of such compounds as  $\text{CaO} \cdot 2\text{POCl}_3$  lends some support to the view that even in compounds like apatite and wagnerite the halogen is directly attached to phosphorus. We are seeking further evidence in favour of this view.

We hope to discuss the precise nature of the compounds of phosphoryl chloride and pyrophosphoryl chloride in another paper, as well as the mechanism of the reaction between phosphoryl chloride and metallic oxide which leads to the formation of metallic chloride in certain cases.

#### EXPERIMENTAL.

##### *Reactions between Oxides and Phosphoryl Chloride.*

In the following experiments the freshly ignited oxide was added to excess of freshly distilled phosphoryl chloride. The mixture enclosed in a sealed tube was, except when otherwise stated, heated to  $110^\circ$  in an oil-bath until examination showed that the oxide had reacted completely. The crystalline solid was then collected, and drained on porous plate in a desiccator containing potassium hydroxide and sulphuric acid until dry and powdery. In all these operations precautions were taken to exclude moisture as far as possible.

$\text{CaO} \cdot 2\text{POCl}_3$ .—The quantities of lime and phosphoryl chloride

employed averaged about 0.56 gram and 10 c.c. respectively. The lime was gradually converted into a crystalline powder consisting of small, rectangular prisms. The length of time required for this transformation varied considerably, but was never less than two days at 110°. The following analyses refer to different preparations:

Found:  $\text{CaO}=16.16, 16.22, 15.15$ ;  $\text{P}_2\text{O}_5=38.62, 39.33, 39.92$ ;  
 $\text{Cl}=58.58, 56.16, 57.89$ .

$\text{CaO}, 2\text{POCl}_3$  requires  $\text{CaO}=15.43$ ;  $\text{P}_2\text{O}_5=39.1$ ;  $\text{Cl}=58.64$  per cent.

From the appearance of the crystals formed, it is clear that the compound  $\text{CaO}, 2\text{POCl}_3$  is also formed when lime and phosphoryl chloride interact at 25° or at the room temperature, but the change taking place very slowly under these conditions has not time for completion before a further change sets in. This causes the contents of the tube to become pasty, owing to the formation of a very fine solid. We have not been able to obtain satisfactory analyses of this solid owing to the difficulty of separating it from the excess of phosphoryl chloride, but those we have made point to the formation of a compound  $\text{CaO}, 3\text{POCl}_3$ .

The compound  $\text{CaO}, 2\text{POCl}_3$  is exceedingly sensitive to moisture, and dissolves at once in water, yielding a strongly acid solution.

$\text{MgO}, 2\text{POCl}_3$  and  $\text{MgO}, 3\text{POCl}_3$ .—Magnesium oxide reacts far more readily with phosphoryl chloride than does lime, which is probably chiefly due to the fact that the magnesium compound is markedly soluble in phosphoryl chloride, whereas the calcium compound is insoluble.

On heating magnesium oxide and phosphoryl chloride in a sealed tube to 110°, one of two things may happen: either the oxide is slowly converted into a crystalline compound without any marked evidence of solution, or else practically all the oxide may dissolve. The solution obtained in the latter case deposits large (5 mm.) and well defined crystals on cooling, although it may remain supersaturated for a considerable time.

The compound obtained in the first case consists of  $\text{MgO}, 2\text{POCl}_3$ , and in the second case of  $\text{MgO}, 3\text{POCl}_3$ .

Which course the reaction takes seems to be more or less a matter of accident:

Found:  $\text{MgO}=11.14$ ;  $\text{P}_2\text{O}_5=42.38$ ;  $\text{Cl}=62.95$ .

$\text{MgO}, 2\text{POCl}_3$  requires  $\text{MgO}=11.60$ ;  $\text{P}_2\text{O}_5=40.88$ ;  
 $\text{Cl}=61.33$  per cent.

Found:  $\text{MgO}=7.8$ ;  $\text{P}_2\text{O}_5=43.2$ ;  $\text{Cl}=63.2$ .

$\text{MgO}, 3\text{POCl}_3$  requires  $\text{MgO}=8.07$ ;  $\text{P}_2\text{O}_5=42.52$ ;  
 $\text{Cl}=63.79$  per cent.



The phosphoryl chloride in these compounds is relatively loosely held. It can be slowly removed by simply washing with light petroleum or by the action of heat. Then again the chemical behaviour of the compounds described is very similar to that of phosphoryl chloride itself. Thus, when the compound  $\text{CaO}, 2\text{POCl}_3$  is treated with moist air or alcohol, all the chlorine is removed as hydrogen chloride; whilst one molecule of  $\text{CaO}, 2\text{POCl}_3$  reacts with 8 molecules of aniline or 12 molecules of ammonia just as two molecules of phosphoryl chloride would.

From this behaviour it is to be concluded that the compounds described in this paper belong to that large group of compounds called, somewhat vaguely, "molecular compounds."

$\text{MnO}, 3\text{POCl}_3$ .—Manganous oxide is slowly converted into a very pale pink substance when heated to  $110^\circ$  with phosphoryl chloride. This seems to consist chiefly of manganous chloride with a considerable amount of the compound  $\text{MnO}, 3\text{POCl}_3$ . The latter is sparingly soluble in phosphoryl chloride, which renders its separation from the manganous chloride possible. The mixture of manganous oxide and phosphoryl chloride is sealed up in a fairly long, stout tube bent at an angle of about  $90^\circ$ . The materials are heated in one limb to  $110^\circ$  until the liquid is saturated, when it is carefully decanted into the other limb, where, on cooling, crystals of the compound  $\text{MnO}, 3\text{POCl}_3$  are deposited. The liquid is then poured back into the other limb and again saturated, and these processes continued until sufficient crystals have accumulated. The tube is then opened, and the solid products separated for analysis. It is not easy to obtain more than a small quantity of the compound in this way, and owing to the smallness of the crystals the difficulty of separating and handling it is intensified. The result is that a considerable amount of moisture is almost inevitably absorbed, so that the analyses are not very satisfactory:

Found:  $\text{MnO} = 13.14$ ;  $\text{P}_2\text{O}_5 = 41.3$ ;  $\text{Cl} = 53.52$ .

$\text{MnO}, 3\text{POCl}_3$  requires  $\text{MnO} = 13.35$ ;  $\text{P}_2\text{O}_5 = 40.08$ ;

$\text{Cl} = 60.12$  per cent.

After allowing for the oxygen-equivalent of the chlorine there is a deficit of 4.44 per cent. due to moisture absorbed during the handling and in the desiccator, this moisture being partly present as such, and having partly reacted with the chlorine to evolve hydrogen chloride.

During one experiment the formation of large, pink crystals was observed at one stage. These were not, however, separated, and could not be obtained again. They very possibly consisted of the compound  $\text{MnO}, 2\text{POCl}_3$ , for we have obtained a beautiful ethyl

acetate derivative of this compound,  $\text{MnO}, \text{P}_2\text{O}_5\text{Cl}_4, 2\text{C}_4\text{H}_8\text{O}_2$ , which will be described presently.

*Action of Phosphoryl Chloride on Zinc Oxide.*—Large amounts of zinc oxide will dissolve in phosphoryl chloride at the ordinary temperature with considerable ease. If the phosphoryl chloride be in moderate excess, about ten days are required for complete solution; the less the excess of phosphoryl chloride the longer is the time required, and the more viscous is the resulting clear solution. When the reagents were mixed in the proportion of one molecule of zinc oxide to two of phosphoryl chloride, and the tube left on its side so as to bring a large surface of the oxide in contact with the liquid, a homogeneous solution which was so viscous as almost to constitute a glass was obtained after six months.

A mixture in the proportion of one molecule of zinc oxide to three of phosphoryl chloride had, after three months, deposited crystals consisting chiefly of small, rhombic plates, possibly mixed with some of another kind. The solution, originally viscous, was now quite mobile.

Analysis of the crystals gave:

Found:  $\text{ZnO} = 22.40$ ;  $\text{P}_2\text{O}_5 = 32.86$ ;  $\text{Cl} = 56.81$ .

Allowing for the oxygen equivalent of the chlorine, we have  $12.07 - 12.80 = 99.27$ , showing a deficit (moisture) of 0.73 per cent.

This corresponds very closely with a mixture of 76.93 per cent. of the compound  $\text{ZnO}, 3\text{POCl}_3$  and 23.07 per cent. of zinc chloride.

The action of heat on the clear solutions of zinc oxide in phosphoryl chloride is somewhat peculiar. On raising the temperature they become turbid, and gradually separate into two liquid layers, the lower of which is more viscous than the other. The temperature at which this separation begins depends on the concentration of the zinc oxide. The greater the concentration the lower is the temperature required. If too little zinc oxide is present, no separation may occur, even at  $100^\circ$ . With one gram of zinc oxide in about 15 grams of phosphoryl chloride, separation into two layers began at  $56^\circ$ . On gradually raising the temperature, while more and more of the lower viscous layer separated, it at the same time gave off bubbles of the more mobile liquid, and became in consequence still more viscous. The mutual solubility of the two liquids clearly diminishes with rise of temperature; on cooling, the two again mix completely.

An experiment was performed in which a solution of zinc oxide in phosphoryl chloride was heated to  $100^\circ$  in a wide tube sealed at one end to a narrow one. The tube was held vertically, so that the viscous liquid collected in the narrow part. When separation

was complete, the tube was removed from the bath, and inverted to separate the mobile from the viscous liquid. The latter on cooling became almost a glass, and the portion of the tube containing it was cut off. It was weighed, and the contents analysed:

Found:  $\text{ZnO} = 21.24$ ;  $\text{P}_2\text{O}_5 = 36.45$ ;  $\text{Cl} = 54.61$ .  
 $\text{ZnO} \cdot 2\text{POCl}_3$  requires  $\text{ZnO} = 20.96$ ;  $\text{P}_2\text{O}_5 = 36.60$ ;  $\text{Cl} = 54.81$  per cent.

It is doubtful whether such a product can be regarded as a definite compound.

*Action of Phosphoryl Chloride on Other Oxides.*—Cadmium, cobaltous, cupric, cuprous, mercuric, ferric, and aluminium oxides all react with phosphoryl chloride, both at the ordinary temperature and when heated to  $100^\circ$ , but the rate of reaction is in most cases slow, and varies considerably. In all cases the colour of the product formed is that of the anhydrous chloride, of which it seems chiefly composed. We have only actually separated and analysed the solid in the case of cadmium and cupric oxides. In the case of ferric oxide a large amount dissolves in the phosphoryl chloride, which becomes dark reddish-brown.

Owing to the difficulty of separation, the analysis of the cadmium product was not satisfactory, but was sufficient to show that one was dealing with a mixture containing a large percentage of cadmium chloride.

The product obtained from cupric oxide could be more easily handled, and two experiments gave the following analytical results:

Found:  $\text{CuO} = 46.96, 55.51$ ;  $\text{P}_2\text{O}_5 = 14.31, 16.36$ ;  $\text{Cl} = 46.54, 37.51$ .

The second experiment was carried out in a sealed tube, and several weeks were required for all the oxide to react. The analysis corresponds closely with a mixture of 25.48 per cent. of copper metaphosphate\* and 74.52 per cent. of cupric chloride, although there is slightly too much copper, probably present as unaltered oxide.

In the first experiment, which was carried out in a flask fitted with ground-in air condenser and calcium chloride drying tube, the reaction only required twenty-four hours, but the analysis shows a deficit of 2.77 per cent. If this is regarded as moisture which has replaced chlorine by hydroxyl, the analytical figures would indicate a mixture of 38.97 per cent. of the compound  $\text{CuO} \cdot 2\text{POCl}_3$  and 61.03 per cent. of cupric chloride.

*Compounds of the Type  $\text{MO} \cdot \text{P}_2\text{O}_5\text{Cl}_2 \cdot 2\text{X}$*  (where X = the organic

\* On treating the product with water a slate-coloured solid (probably the metaphosphate) separated, which only dissolved slowly after the addition of nitric acid.

solvent).—These were all obtained by adding the freshly ignited oxide to a solution of phosphoryl chloride in the organic liquid, which had been dried over calcium chloride and freshly distilled. It is best to only use a little more than two molecules of phosphoryl chloride to one of oxide. Solution was assisted when necessary by gentle heating, the mixture being contained in a flask with ground-in air condenser closed by a calcium chloride tube. The solution was then allowed to crystallise in a desiccator containing solid potassium hydroxide and concentrated sulphuric acid. The crystals separating were washed with a small quantity of the solvent, drained on porous plate in the desiccator, and analysed. Under these conditions sufficient moisture was present in the solvent or absorbed during the experiment to effect the displacement of the two atoms of chlorine. The hydrogen chloride thus formed can be absorbed and estimated, as was actually done in one or two cases. On solution in water these compounds are completely decomposed with separation of the organic portion of the molecule—which in a few cases was directly estimated. As a rule, however, it was obtained by difference.

$\text{CaO}, \text{P}_2\text{O}_5\text{Cl}_4, 2(\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3)$ .—This forms beautiful transparent crystals several mm. long, which are sparingly soluble in cold acetone. During the preparation of this compound the solution becomes brown owing to the condensing action of the liberated hydrogen chloride on the acetone. By carefully washing the crystals they can be obtained colourless, and then keep fairly well in a sealed tube. If not properly washed they soon become brown:

Found:  $\text{CaO} = 13.73, 13.48$ ;  $\text{P}_2\text{O}_5 = 33.23, 34.20$ ;  $\text{Cl} = 33.13, 34.08$ ;  
 $\text{C}_3\text{H}_6\text{O}$  (by diff.) =  $27.37, 25.92$ .  
 $\text{CaO}, \text{P}_2\text{O}_5\text{Cl}_4, 2\text{C}_3\text{H}_6\text{O}$  requires  $\text{CaO} = 13.21$ ;  $\text{P}_2\text{O}_5 = 33.49$ ;  $\text{Cl} = 33.45$ ;  
 $\text{C}_3\text{H}_6\text{O} = 27.39$  per cent.

In the second experiment the crystals had been left for forty-eight hours in an evacuated desiccator containing sulphuric acid, and had evidently lost a little acetone.

$\text{MnO}, \text{P}_2\text{O}_5\text{Cl}_4, 2(\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3)$ .—In this case a considerable amount of manganous chloride is formed, from which the acetone solution must be decanted. On crystallisation, small prisms of a pale pink colour are obtained. The analysis is not very satisfactory, probably owing to the presence of a certain amount of manganous chloride:

Found:  $\text{MnO} = 16.44$ ;  $\text{P}_2\text{O}_5 = 31.66$ ;  $\text{Cl} = 33.14$ ;  $\text{C}_3\text{H}_6\text{O}$  (by diff.) =  $26.24$ .  
 $\text{MnO}, \text{P}_2\text{O}_5\text{Cl}_4, 2\text{C}_3\text{H}_6\text{O}$  requires  $\text{MnO} = 16.78$ ;  $\text{P}_2\text{O}_5 = 33.59$ ;  
 $\text{Cl} = 33.55$ ;  $\text{C}_3\text{H}_6\text{O} = 23.65$  per cent.

$\text{CaO}, \text{P}_2\text{O}_5\text{Cl}_4, 2(\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3)$ .—This compound crystallises readily in long prisms, only sparingly soluble in cold ethyl acetate:

Found:  $\text{CaO}=11\cdot69$ ;  $\text{P}_2\text{O}_5=29\cdot57$ ;  $\text{Cl}=29\cdot14$ ;  $\text{C}_4\text{H}_8\text{O}_2$  (by diff.)  $=36\cdot27$ .

$\text{CaO}, \text{P}_2\text{O}_5\text{Cl}_4, 2\text{C}_4\text{H}_8\text{O}_2$  requires  $\text{CaO}=11\cdot57$ ;  $\text{P}_2\text{O}_5=29\cdot34$ ;  
 $\text{Cl}=29\cdot31$ ;  $\text{C}_4\text{H}_8\text{O}_2=36\cdot39$  per cent.

$\text{MgO}, \text{P}_2\text{O}_5\text{Cl}_4, 2(\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3)$ .—This was prepared in just the same way as the calcium compound. The ethyl acetate solution has, however, a marked tendency to remain supersaturated. Fine crystals can be obtained, very similar to, but larger than, those of the calcium compound. The prisms are fairly broad, and may be from 0.5 to 1.0 cm. long:

Found:  $\text{MgO}=8\cdot55, 8\cdot56$ ;  $\text{P}_2\text{O}_5=30\cdot57, 28\cdot84$ ;  $\text{Cl}=30\cdot70, 30\cdot48$ ;  
 $\text{C}_4\text{H}_8\text{O}_2$  (by diff.)  $=37\cdot10, 39\cdot00$ .

$\text{MgO}, \text{P}_2\text{O}_5\text{Cl}_4, 2\text{C}_4\text{H}_8\text{O}_2$  requires  $\text{MgO}=8\cdot74$ ;  $\text{P}_2\text{O}_5=30\cdot32$ ;  
 $\text{Cl}=30\cdot28$ ;  $\text{C}_4\text{H}_8\text{O}_2=37\cdot59$  per cent.

The second analysis refers to a preparation obtained from the action of ethyl acetate on previously prepared  $\text{MgO}, 3\text{POCl}_3$ .

$\text{MnO}, \text{P}_2\text{O}_5\text{Cl}_4, 2(\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3)$ .—A small quantity of manganous chloride is commonly formed in this preparation, from which the solution is decanted into the crystallising dish. The compound forms magnificent pink prisms, somewhat resembling cubes, and several mm. long:

Found:  $\text{MnO}=14\cdot25$ ;  $\text{P}_2\text{O}_5=28\cdot34$ ;  $\text{Cl}=28\cdot76$ ;  $\text{C}_4\text{H}_8\text{O}_2$  (by diff.)  $=35\cdot11$ .

$\text{MnO}, \text{P}_2\text{O}_5\text{Cl}_4, 2\text{C}_4\text{H}_8\text{O}_2$  requires  $\text{MnO}=14\cdot22$ ;  $\text{P}_2\text{O}_5=28\cdot48$ ;  
 $\text{Cl}=28\cdot44$ ;  $\text{C}_4\text{H}_8\text{O}_2=35\cdot27$  per cent.

This compound is clearly derived from the compound  $\text{MnO}, 2\text{POCl}_3$ , although we have not actually obtained that compound itself.

$\text{CaO}, \text{P}_2\text{O}_5\text{Cl}_4, 2(\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_5)$ .—This is a white compound, crystallising in small prisms, moderately soluble in hot ethyl benzoate. On solution of the solid in water, the ester, being insoluble, separates out. It was collected, dissolved in ether, the ethereal solution washed and dried, the ether driven off, and the residual ester weighed:

Found:  $\text{CaO}=8\cdot50$ ;  $\text{P}_2\text{O}_5=22\cdot21$ ;  $\text{Cl}=20\cdot88$ ;  $\text{C}_8\text{H}_{10}\text{O}_2=50\cdot0$  (by diff.)  $=55\cdot46$ .

$\text{CaO}, \text{P}_2\text{O}_5\text{Cl}_4, 2\text{C}_8\text{H}_{10}\text{O}_2$  requires  $\text{CaO}=9\cdot21$ ;  $\text{P}_2\text{O}_5=23\cdot35$ ;  
 $\text{Cl}=23\cdot32$ ;  $\text{C}_8\text{H}_{10}\text{O}_2=49\cdot34$  per cent.

The solid analysed contained a small quantity of adhering ester, which it is impossible to remove completely on porous plate. On this account, in the following preparation of the methyl derivative

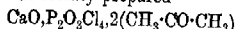
the free ester was removed by distillation at  $100^{\circ}$  in a Töpler vacuum.



Found:  $\text{CaO}=9\cdot75$ ;  $\text{P}_2\text{O}_5=24\cdot97$ ;  $\text{Cl}=23\cdot25$ ;  $\text{C}_6\text{H}_5\text{O}_2$  (by diff.)  $=47\cdot27$ .

$\text{CaO}, \text{P}_2\text{O}_5\text{Cl}_4, 3\text{C}_6\text{H}_5\text{O}_2$  requires  $\text{CaO}=9\cdot66$ ;  $\text{P}_2\text{O}_5=24\cdot48$ ;  $\text{Cl}=24\cdot45$ ;  $\text{C}_6\text{H}_5\text{O}_2=46\cdot90$  per cent.

*Recrystallisation of  $\text{CaO}, \text{P}_2\text{O}_5\text{Cl}_4, 2(\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3)$  from Ethyl Acetate.*—One gram of freshly prepared



was dissolved by the aid of heat in about 15 c.c. of freshly distilled ethyl acetate. On cooling, there was an abundant separation of crystals, which on analysis gave the following figures, showing that they consisted of the ethyl acetate compound:

Found:  $\text{CaO}=12\cdot02$ ;  $\text{P}_2\text{O}_5=29\cdot97$ ;  $\text{Cl}=29\cdot33$ ;  $\text{C}_4\text{H}_8\text{O}_2$  (by diff.)  $=35\cdot29$ .

$\text{CaO}, \text{P}_2\text{O}_5\text{Cl}_4, 2\text{C}_4\text{H}_8\text{O}_2$  requires  $\text{CaO}=11\cdot57$ ;  $\text{P}_2\text{O}_5=29\cdot34$ ;  $\text{Cl}=29\cdot31$ ;  $\text{C}_4\text{H}_8\text{O}_2=36\cdot39$  per cent.

A similar experiment to the above was carried out, starting with the ethyl acetate compound, and recrystallising it from acetone. Crystals of the acetone compound resulted.

*Experiments with Diethyl Oxalate and Ethyl Trichloroacetate.*

It has already been mentioned (p. 1405) that from the behaviour of mixtures of lime and phosphoryl chloride at  $25^{\circ}$  it is probable that a compound,  $\text{CaO}, 3\text{POCl}_3$ , is finally formed at that temperature by continued action of an excess of phosphoryl chloride on the compound  $\text{CaO}, 2\text{POCl}_3$  formed first of all.

The existence of the compound  $\text{CaO}, 3\text{POCl}_3$  has been confirmed by experiments carried out in presence of diethyl oxalate or ethyl trichloroacetate.

Lime dissolves fairly readily in a mixture of phosphoryl chloride and either of these esters when heated to  $110^{\circ}$ . It is advisable to use about ten parts by weight of phosphoryl chloride and thirty parts of ester to one part of lime. Solution of the lime is complete in about twenty-four hours, and on cooling well formed crystals slowly separate. About a week was required for complete separation from the oxalate solution, which yielded brilliant, rhombohedral prisms about 2 mm. long. Unfortunately, in spite of their appearance, these crystals did not consist of one compound only. It seems clear that what happens is as follows: First of all, either the compound  $\text{CaO}, 2\text{POCl}_3$  or  $\text{CaO}, 3\text{POCl}_3$  or a mixture of both is formed, according to the concentrations employed. Under the

influence of any traces of moisture present the oxalic ester derivative of the compound  $\text{CaO}, \text{P}_2\text{O}_3\text{Cl}_4$  is formed from the compound  $\text{CaO}, 2\text{POCl}_3$ . Moisture also acts on the compound  $\text{CaO}, 3\text{POCl}_3$ , replacing chlorine by hydroxyl, with formation of compounds incapable of combining with organic esters, etc. It seems certain that the power of adding on these organic molecules is confined to the compounds of the general formula  $\text{MO}, \text{P}_2\text{O}_3\text{Cl}_4$ .

The results obtained in presence of oxalic and trichloroacetic esters can be explained in this way, but, owing to the complicated nature of the problem, it is unnecessary to give more than one analysis, and that mainly to show that the compound  $\text{CaO}, 3\text{POCl}_3$  is formed. The analysis refers to a well crystallised preparation from an oxalic ester experiment:

Found:  $\text{CaO} = 10.00$ ;  $\text{P}_2\text{O}_5 = 37.10$ ;  $\text{Cl} = 52.25$ ;  $\text{C}_6\text{H}_{10}\text{O}_4$  (by titration with  $\text{KMnO}_4$ )  $= 5.19$ ;  $\text{H}_2\text{O}$  (by diff.)  $= 7.23$ .  
 $\text{Ca}:\text{P} = 1:2.92$ .

#### *Reaction between Lime and Phosphoryl Chloride in Presence of Ether.*

In absolute ether lime reacts slowly with phosphoryl chloride to give the compound  $\text{CaO}, 2\text{POCl}_3$ . This conversion can be effected in a sealed tube at  $25^\circ$  in somewhat longer than three weeks. A tube sealed up for that length of time gave a solid, which on analysis gave the following analytical figures:

Found:  $\text{CaO} = 17.42$ ;  $\text{P}_2\text{O}_5 = 37.15$ ;  $\text{Cl} = 52.11$ . Deficit (ether)  $= 5.08$ .

Ratio:  $\text{Ca}:\text{P}:\text{Cl}:\text{Ether} = 1.24:2.08:5.88:0.28$ .

Even with the above precautions a small quantity of the compound  $\text{CaO}, \text{P}_2\text{O}_3\text{Cl}_4, 2\text{C}_4\text{H}_{10}\text{O}$  appears to have been formed. The lime, moreover, is not completely converted.

If the reaction is carried out in a flask fitted with air condenser, and no special precautions are taken to ensure that the ether is absolutely free from moisture, the reaction occurring is much more energetic, the ether being sometimes caused to boil. Under these conditions larger proportions of the pyrophosphoryl chloride derivative are obtained; some of the compound  $\text{CaO}, 2\text{POCl}_3$  is, however, always present, and owing, moreover, to the fact that the ether compound begins to separate before all the lime has passed into solution it is difficult to obtain a pure product. The best preparation of the ether compound which we have obtained was got by the continued action of ether on an oxalic ester preparation. The final product of the action of ether consisted of small, brilliant rhombohedra. On solution in water it was evident that the crystals

contained considerable quantities of ether, although titration with permanganate showed that about 10 per cent. of the organic portion of the molecule was oxalic ester and not ether:

Found:  $\text{CaO}=12.57$ ;  $\text{P}_2\text{O}_5=31.20$ ;  $\text{Cl}=29.51$ ;  $\text{C}_6\text{H}_{10}\text{O}_4=2.66$ ;  
 $\text{C}_4\text{H}_{10}\text{O}$  (by diff.)  $=30.71$ .

$\text{CaO}, \text{P}_2\text{O}_5\text{Cl}_4, 2\text{C}_4\text{H}_{10}\text{O}$  requires  $\text{CaO}=12.28$ ;  $\text{P}_2\text{O}_5=31.14$ ;  
 $\text{Cl}=31.11$ ;  $\text{C}_4\text{H}_{10}\text{O}=32.45$  per cent.

*Reactions of Zinc, Cadmium, Cobaltous, and Cupric Oxides with Phosphoryl Chloride in Presence of Ethyl Acetate.*

We have been unable to obtain any crystalline organic derivatives from the interaction of zinc oxide, phosphoryl chloride, and ethyl acetate.

In the case of cadmium oxide a white powder, seen to be crystalline under the microscope, was formed. It was quite insoluble in ethyl acetate, and the analysis gave the following figures:

	$\text{CdO}$ .	$\text{P}_2\text{O}_5$ .	$\text{Cl}$ .	Ethyl acetate (by diff.).
Expt. I. ....	57.20	5.48	33.35	11.49
Expt. II. ....	49.11	7.25	31.96	18.88

The white solid is evidently a mixture of the compound  
 $\text{CdO}, \text{P}_2\text{O}_5\text{Cl}_4, 2(\text{C}_4\text{H}_8\text{O}_2)$

and cadmium chloride (the latter apparently being combined with a variable amount of ethyl acetate of crystallisation). Experiment I, for example, can be apportioned as follows:

As  $\text{CdO}, \text{P}_2\text{O}_5\text{Cl}_4, 2(\text{C}_4\text{H}_8\text{O}_2) \dots \text{CdO}=4.94$ ;  $\text{P}_2\text{O}_5=5.48$ ;  $\text{Cl}=5.48$ ;  
 $\text{C}_4\text{H}_8\text{O}_2=6.78$ , leaving (by difference) as  $\text{CdCl}_2 \dots \text{CdO}=52.26$ ;  
 $\text{Cl}=27.87$ ;  $\text{C}_4\text{H}_8\text{O}_2=4.71$  per cent.

Atomic ratio:  $\text{Cd}:\text{Cl}$  in the latter  $=1:1.93$ .

The reaction between cobaltous oxide, phosphoryl chloride, and ethyl acetate leads to the formation of a blue solution, from which nothing could be crystallised suitable for analysis, and of a blue solid which was simply cobalt chloride combined with some ethyl acetate.

With cupric oxide the course of the reaction is somewhat similar to that followed in the case of cadmium oxide. If large quantities of cupric oxide and phosphoryl chloride, in proportion to the ethyl acetate, are used, the reaction may be very vigorous. No copper passes into solution. The solid product appears to be more complex than in other cases, and is probably a mixture of the compounds  $\text{CuP}_2\text{O}_6$ ,  $\text{CuO}, \text{P}_2\text{O}_5\text{Cl}_4, 2(\text{C}_4\text{H}_8\text{O}_2)$ , and cupric chloride (combined with some ethyl acetate), as evidenced by the following analytical figures:



	CuO.	P <sub>2</sub> O <sub>5</sub> .	Cl.	Ethyl acetate (by diff.).
Expt. I. ....	38.88	24.58	33.59	10.52
Expt. II. ....	39.33	14.58	35.51	18.58

In conclusion, we wish to thank Messrs. R. Kingan, F. O. Rice, and E. T. Williams for assistance in preparing some of the compounds described above.

WILLIAM GOSSAGE LABORATORY,  
UNIVERSITY OF LIVERPOOL.

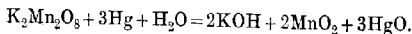
### CLIX.—*Some Reducing Actions of Mercury.*

By DAVID BORAR.

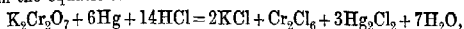
It is stated by Kirchman (*Arch. Pharm.*, 1872, **200**, 203) that mercury is oxidised when agitated with a solution of potassium permanganate, mercurous oxide being formed if the solution is cold, and mercuric oxide if the solution is hot. At the suggestion of Dr. E. P. Perman I have investigated the action of mercury on potassium permanganate and on a number of other substances.

In all the experiments the solutions were agitated with mercury in a stoppered bottle, and at the ordinary room temperature unless otherwise stated. The mercury used was purified by the ordinary methods, and no doubt contained traces of other metals.

*Potassium Permanganate.*—No action takes place between dry potassium permanganate and mercury. In the presence of water, however, reduction of the permanganate takes place readily. With excess of mercury the reduction is complete, and the amount of potassium hydroxide formed from a known amount of permanganate was determined by titration with standard acid. Experiments were also made in which permanganate was in excess, and the amount required to oxidise a given weight of mercury was determined. The results of these experiments show that all the potassium in the permanganate is converted into potassium hydroxide, part of which seems to form adsorption compounds or unstable manganites with the manganese dioxide formed. As a mean of three experiments it was found that 1 gram of mercury reduces 0.519 gram of permanganate. These results indicate that the reaction between mercury and potassium permanganate takes place in accordance with the equation:



*Potassium Dichromate.*—Mercury does not reduce neutral solutions of potassium dichromate to any extent measurable by ordinary analytical methods. In the presence of hydrochloric acid, however, reduction takes place readily. Experiments were made in which excess of mercury was used, and others in which excess of dichromate was taken. The former showed that the dichromate was completely reduced to chromium chloride, and the latter that the amount of dichromate reduced by a given weight of mercury was constant providing that too large a quantity of hydrochloric acid was not taken. It was found as a mean of five experiments that 1 gram of mercury reduces 0.2452 gram of dichromate. The precipitate obtained in the various experiments was tested for mercurous chromate and mercuric chloride, neither of which could be detected, and the precipitate was found to consist of mercurous chloride only. From the equation:



1 gram of mercury reduces 0.2456 gram of dichromate. The number found by experiment is in good agreement with this number. Hence the equation given probably represents the reaction which takes place.

*Ferric Salts.*—A solution of ferric chloride in water is readily reduced by mercury. Iron alum in the presence of hydrochloric acid is also reduced, but without the addition of hydrochloric acid reduction does not take place to any extent. Using mercury as reducing agent and titrating with standard dichromate in the usual way, the amount of iron in iron alum is found to be 11.61 per cent. The theoretical number is 11.59 per cent.

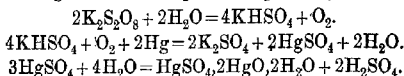
The amount of iron in hematite was determined by using mercury as reducing agent, and again using stannous chloride as reducing agent. The amount found was 91.30 per cent. by the first, and 91.16 per cent. by the second method.

Reduction takes place rapidly, especially if the solution is heated to 60–70°. The precipitate of mercurous chloride which forms during the process settles down rapidly from the hot solution, leaving the liquid clear. The presence, however, of comparatively large quantities of mercurous chloride does not affect the titrations appreciably.

The results obtained show that mercury may well be employed as a reducing agent for ferric compounds in the estimation of iron, and this method is less troublesome than the usual methods.

*Potassium Persulphate.*—On shaking a cold solution of potassium persulphate with mercury a slight, black precipitate was first formed, and then a white precipitate, which slowly changed to a lemon-yellow colour on keeping. The solution became acid, and

potassium sulphate remained in solution. In a hot solution, however, the yellow precipitate was formed almost immediately. This precipitate was insoluble in water, but soluble in dilute sulphuric acid. It decomposed on heating into mercury, oxygen, and sulphur dioxide. Mercuric sulphate readily gives the yellow basic sulphate with water, whereas mercurous sulphate does not, even on boiling. Hence the changes which take place are probably as follows:



*Copper Sulphate.*—A fairly good yield of cuprous chloride was obtained by shaking mercury with copper sulphate solution and excess of hydrochloric acid.

*Nitrobenzene.*—Mercury in the presence of hydrochloric acid was found to reduce nitrobenzene to aniline, but only to a small extent, even on heating.

The action of mercury was also tried on potassium nitrate in neutral and in acid solution, but no change could be detected. Solutions of potassium chlorate and sodium peroxide also had no action on mercury.

After the work of which this paper gives a brief account had been completed, my attention was called to a paper by Carnegie (*Trans.*, 1888, **53**, 471) on the reduction of ferric salts by finely divided metals. Carnegie found that many metals, amongst them mercury, will reduce solutions of ferric salts, but does not point out that mercury can be used conveniently and possibly with advantage in the estimation of iron in ferric compounds. Previous work on the action of potassium permanganate on mercury, for example, that by Giles (*Chem. News*, 1867, **15**, 204), does not appear to have been carried out quantitatively.

In conclusion, my best thanks are due to Dr. E. P. Perman for many helpful suggestions and advice.

UNIVERSITY COLLEGE,  
CARDIFF.

LX.—*Electromotive Forces in Alcohol. Part I.*  
*Concentration Cells with Electrodes Reversible to*  
*Chlorine Ions.*

By ARTHUR LAPWORTH and JAMES RIDDICK PARTINGTON.

THE work described in the present paper was begun in connexion with the study of equilibria between electrolytes in alcohol, and in particular of the equilibrium between mineral acids, alcohol, and water.

The potential differences which it was desired to estimate being comparatively small ones, it was necessary, in the first instance, to ascertain whether it was possible to obtain consistent results with concentration cells, reproducible within not more than two or three millivolts, when anhydrous alcohol was used as cell liquid. The experiments were carried out with dissolved hydrogen chloride as electrolyte, for it was necessary to know as nearly as possible the transport numbers of its ions, for experiments to be undertaken later with the hydrogen electrode.

Numerous instances of measurements of potential differences in alcohol are to be found in the literature, but the few which appeared to bear directly on the points in question showed certain discrepancies which led us to re-investigate the subject. The following records are the most pertinent to the present inquiry.

Cattaneo (*Atti R. Accad. Lincei*, 1897, [v], 6, i, 279) determined by Hittorf's method, the transport numbers for the chlorine ions in solutions of hydrogen chloride in various solvents, and obtained the following results:

In water, 0.224; ethyl alcohol, 0.205; methyl alcohol, 0.236; amyl alcohol, 0.240; glycerol, 0.237; ethyl alcohol+chloroform, 0.209; ethyl alcohol+ether, 0.218.

This worker compared these with the number 0.214 calculated by Kohlrausch from Hittorf's results with aqueous hydrochloric acid, and drew the conclusion that the influence of the solvent was almost inappreciable. More recent determinations, however, have shown that the value 0.214 for aqueous solution is considerably too high. Thus Bein (*Zeitsch. physikal. Chem.*, 1898, 21, 1) obtained the value 0.166, Bogdan (*ibid.*, 1901, 37, 673) 0.174, and Joachim (*Diss.*, Berlin, 1905) 0.167, whilst the results of Noyes and Sammet (*Zeitsch. physikal. Chem.*, 1903, 43, 49) point to a value very close to 0.167 as the correct one (compare also Noyes and Kato (*J. Amer. Chem. Soc.*, 1908, 30, 318)). The conclusion drawn by Cattaneo thus appears to have a slender foundation.

Campetti (*Jahrb. Elektrochem.*, 1895, 1, 22) determined the transport numbers of the anions in solutions of lithium chloride and silver nitrate in water, methyl alcohol, and ethyl alcohol. The values obtained for the former salt being 0.705, 0.64, and 0.700 respectively in these solvents.

Carrara (*Gazzetta*, 1896, 26, i, 19; 1903, 33, i, 241; compare also *Jahrb. Elektrochem.*, 1897, 3, 12 and 13) obtained limiting values for conductivities of numerous salts, in water and in methyl alcohol, which were independent of concentration. Using Campetti's values for transport numbers in methyl alcohol, the mobilities of numerous ions in this solvent at 25° were calculated, and the following may be recorded here: Li<sup>+</sup>, 27.83; Na<sup>+</sup>, 37.33; K<sup>+</sup>, 46.10; H<sup>+</sup>, 85.53 or 82.5. These were virtually independent of concentration, and their relative values were affected by the change of solvent from water to methyl alcohol, to an extent not exceeding 10 per cent. in any instance.

Dempwolff (*Physikal. Zeitsch.*, 1904, 5, 637) measured by Hittorf's method, and by the electromotive forces of concentration cells, the transport numbers of the ions of the haloid salts of potassium in methyl alcohol, and found throughout much the same behaviour as with aqueous solutions, but the number for the anion was consistently and considerably lower than that for the aqueous solutions.

Völlmer (*Ann. Phys. Chem.*, 1894, [iii], 52, 328) measured with great care the conductivities of a number of salts in ethyl and methyl alcoholic solution. His results show that over the range of temperature followed, the limiting value for a given salt in methyl alcohol and ethyl alcohol at 18° may be calculated roughly from that in water at the same temperature by multiplication with the factors 0.73 and 0.34 respectively. The temperature-coefficients were hardly different from the temperature-coefficients of the fluidities of the respective solvents.

The present authors have experimented with two types of concentration cells containing hydrogen chloride in absolute alcohol as electrolyte; these contained electrodes of mercury and silver respectively, with mercurous chloride and silver chloride as depolarisers.

It was to be anticipated that the use of an easily oxidisable solvent such as alcohol would probably lead to experimental difficulties not met with when water is employed. Nevertheless, it was finally found possible, with the precautions described in the practical section of this paper, to obtain consistent potential differences, and to reproduce these with solutions of given concentrations within three millivolts at most.

The values for the transport numbers of the ions as calculated

from these results showed a very striking divergence from those obtained with aqueous solutions, that for the anion being about 0.35, in contrast to 0.17, as is obtained with aqueous hydrochloric acid. There are, however, many reasons for believing that this result is not very far from the correct one, as the following considerations may serve to show, and these give the authors confidence in recording the results of their experiments at the present juncture.

In the first instance may be cited the results of Carrara already referred to, from which a value for the transport number for chloridion in methyl-alcoholic hydrogen chloride can be calculated as 0.367. It is remarkable that so striking a result should not have attracted considerable interest as having an obvious bearing on the solvate theory; even in the comprehensive treatise of Jahn ("Grundriss der Electrochemie," 1905) the principal numerical results obtained by Carrara are given, but no special attention is drawn to the anomalous value of the relative mobility of the hydrogen ion.

Secondly, the work of Völlmer, already dealt with, on conductivities in absolute ethyl alcohol, probably attained a high degree of accuracy, and his numbers can hardly be explained on any assumption other than that the relative velocities of most ions, in all the salts examined by him, are nearly the same in water, methyl alcohol, or ethyl alcohol, although the absolute velocities are, of course, entirely different. If this be the correct interpretation of his results, then the transport numbers for the ions of the salts are nearly the same in the three solvents, and the absolute value of the mobility of chloridion in ethyl alcohol may be nearly estimated by multiplying the molecular conductivity of lithium or sodium chloride at infinite dilution in that solvent by the transport number of chloridion in water.

The values of  $\lambda_{\alpha}$  obtained by Völlmer for these two salts were:

	$\lambda_{\alpha}$		
	In water at 18°.	In ethyl alcohol at 18°.	In ethyl alcohol. at 25°.
Sodium chloride .....	103.0	35.9	40.7
Lithium chloride .....	96.0	32.1	36.4

The numbers in the last column are calculated by means of the mean temperature-coefficient determined by Völlmer; multiplying these by the transport numbers of chloridion in aqueous solutions of these two salts, namely, 0.600 and 0.661 respectively (Kohlrausch, 1900, 1902), the values 24.4 and 24.10 are obtained for the mobility of chloridion in alcohol at 25°; subtracting the mean of these, namely, 24.25, from 66.5, the value of  $\lambda_{\alpha}$  for alcoholic hydrogen chloride at 25° obtained from measurements recorded in the present

paper, the number 42.25 is obtained for the mobility of the hydrogen ion in anhydrous alcohol, and the transport number for chloridion becomes

$$\frac{24.25}{66.5} = 0.365.$$

Extrapolation from the data given by Goldschmidt and Udby (*Zeitsch. Elektrochem.*, 1901, 15, 5) leads to 75 as the approximate value of  $\lambda_{\infty}$  for alcoholic hydrogen chloride, and applying this in the foregoing manner, the transport number assumes the value 0.323.

Again, using the transport number, 0.71, obtained by Campetti from direct measurements for chloridion in lithium chloride in alcohol, the mobility of chloridion in alcohol at 25° becomes 25.7, and the transport number in alcoholic hydrogen chloride 0.387.

Lastly, it may be added that experiments in this laboratory on the use of the hydrogen electrode in solutions in anhydrous alcohol have given results which point to a value very near 0.32.

#### EXPERIMENTAL.

The absolute alcohol was prepared by distillation from a proved excess of calcium ethoxide in the manner described in a previous communication (Lapworth and Partington, *Trans.*, 1910, 97, 24). Hydrogen chloride, prepared from well-dried salt and sulphuric acid, was passed through two sulphuric acid drying towers into the alcohol contained in a special apparatus of Jena glass, in which all the connexions were made with ground-glass joints. The exit tube of this apparatus was connected with a sulphuric acid drying tower, and the receiving flask was cooled during the absorption of the gas. The entrance tube of this apparatus was provided with a stopcock, and afterwards served as a syphon for withdrawing the solution from the flask which remained in attachment to the drying-tower, so that access of moisture was avoided.

The acid obtained was of approximately normal strength, a nearly decinormal acid being prepared from it by transferring a portion to a similar apparatus and diluting with absolute alcohol. This operation, and the subsequent filling of the electrodes, were performed as rapidly as possible, to avoid entrance of atmospheric moisture.

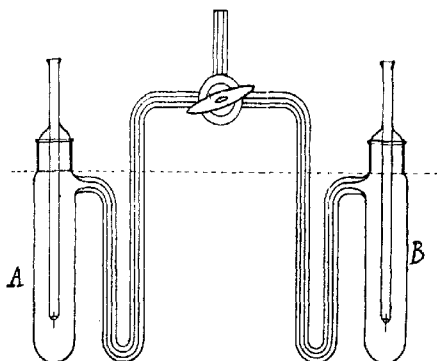
The form of concentration cells used is shown in the figure. Two types were employed:

- (1)  $\text{Hg}, \text{Hg}_2\text{Cl}_2 | [\text{HClAlc.}]_1 || [\text{HClAlc.}]_2, \text{Hg}_2\text{Cl}_2, \text{Hg}.$
- (2)  $\text{Ag}, \text{AgCl} | [\text{HClAlc.}]_1 || [\text{HClAlc.}]_2, \text{Hg}_2\text{Cl}_2, \text{Hg}.$

The tubes *A* and *B* were about 6 cm. long and 1.5 cm. wide. In

the calomel cell the electrodes consisted of platinum wires sealed through glass tubes and dipping under the surface of redistilled mercury. About 0.5 cm. of calomel, previously carefully purified as usual by shaking with water and mercury, washing with alcohol, and drying, was placed over the mercury, and the tubes filled with the alcoholic hydrogen chloride solutions by means of the three-way tap *C*. This tap was greased with vaseline, and kept closed except when a reading was taken. The cell was immersed, to the level shown by the dotted line, in a thermostat at 25°.

In making the cell with silver electrodes, some difficulty was at first experienced in fixing the silver wires, attached to silver plates, in the electrodes, because sealing-wax (which is an admirable material in the case of aqueous solutions) cannot be used in contact



with alcohol. It was found possible, with experience, to cement a silver wire into the constricted part of a glass tube by means of silver chloride fused on with a spirit lamp. The cell was otherwise made up in a manner similar to the calomel cell. In all cases, ground-glass connexions only were used.

The electromotive force measurements were made by means of a potentiometer apparatus consisting of a carefully calibrated platinum-iridium wire with tapping contacts of the same alloy, a Weston normal element, and an Ayrton-Mather moving coil galvanometer. With this apparatus, potential measurements correct to at least 0.5 millivolt could be made.

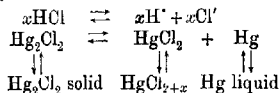
A number of preliminary measurements at the ordinary temperature with commercial absolute alcohol, of about 99.6 per cent. strength, showed that, with the solutions used, cells of the above



types rapidly attained a steady potential, undisturbed by shaking, and reproducible within fairly narrow limits.

In some cases (and also in all cases when perfectly dry alcohol was used) the potential attained a steady value somewhat slowly. This continuous change of potential to a constant final value, doubtless due to slow saturation of the solutions with the depolariser, was totally different from the irregular fluctuation of potential appearing when an electrode is irreversible. These results make it exceedingly probable that electrodes of the types described functionate in a reversible manner.

It was found that with alcoholic solutions of hydrogen chloride of normal strength, the calomel in the cells was rapidly darkened, a change which also occurred, much more slowly, even with decinormal solutions. A portion of the liquid was tested for aldehyde with a negative result, and the reaction is probably analogous to that investigated by T. W. Richards and E. H. Archibald (*Zeitsch. physikal. Chem.*, 1902, **40**, 385) in the case of aqueous solutions, and formulated by them as an equilibrium reaction as follows:



The complex ion  $\text{HgCl}_{2+x}$  is probably  $\text{HgCl}_4^{2-}$  (Le Blanc and Noyes, *ibid.*, 1890, **6**, 389). We found, however, that the darkening of the calomel produced no measurable change in the potential, provided a large excess of unaltered calomel was present. It is interesting to note, however, that the effect is very marked in alcoholic solution with concentrations of hydrogen chloride which in aqueous solution produce very little change, a fact which is probably connected with the greater activity of the acid in alcoholic as compared with aqueous solution.

It was also found that the potential of the silver cell was the same, whether measured in complete darkness, in orange light, or in diffused daylight, although in the latter case a darkening of the silver chloride occurred.

A comparison of results given in detail below indicates that the mean potentials of the calomel and of the silver cells are not markedly different, the former, however, being more regular.

Some experiments were carried out with solutions of hydrogen chloride in absolute alcohol which had not been dried over calcium. The results agreed with those obtained with calcium-dried alcohol, but the potentials assumed a steady value more rapidly in the former case.

Some preliminary experiments have been made with the cells

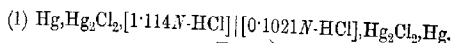
immersed in ice, and the results are given below. In both types of cell the effect of cooling was to produce at first a rise and then a fall of potential, the final value being in some cases slightly greater and in others slightly less than the potential of the cell at 25°. These curious results are possibly connected with the changes of solubility of the depolarisers, leading to a readjustment of equilibrium which occurs only very slowly. Further, the silver chloride is also a colloidal substance, and this would doubtless explain the rather less concordant results obtained with those cells in which it was used.

### Results.

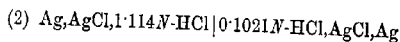
In all cases the first reading was taken about fifteen minutes after setting up the cell.

The time is given in hours after the observations were begun; the potentials are in volts.

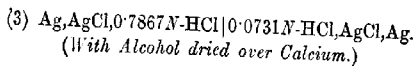
The arrow indicates the direction of the positive current inside the cell.



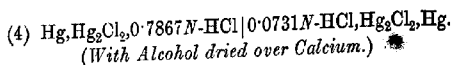
Time.	Potential.	Time.	Potential.
0.00 hours	0.0600 volt		
0.15 "	0.0601 "		Reading taken at 0°.
0.5 "	0.0605 "	25.0 hours	0.0601 volt
2.25 "	0.0604 "		Readings at 25° resumed.
29.0 "	0.0558 "	25.5 hours	0.0619 volt
		50.0 "	0.0602 "



Time.	Potential.	Time.	Potential.
0.0 hours	0.0520 volt		
0.4 "	0.0520 "		Reading taken at 0°.
3.4 "	0.0543 "	29.7 hours	0.0596 volt
23.15 "	0.0536 "		Reading at 25° resumed.
29.4 "	0.0528 "	53.0 hours	0.0576 volt



Time.	Potential.	Time.	Potential.
0.0 hours	0.0417 volt		
17.5 "	0.0466 "	90.0 hours	0.0543 volt
22.0 "	0.0467 "	90.5 "	0.0543 "
25.0 "	0.0502 "		Readings taken at 0°.
43.0 "	0.0543 "	117.75 hours	0.0480 volt
		122.0 "	0.0491 "



Time.	Potential.	Time.	Potential.
0.0 hours	0.0371 volt	71.1 hours	0.0558 volt
3.14 "	0.0418 "	Readings taken at 0°.	
23.64 "	0.0568 "	95.10 hours	0.0567 volt
70.14 "	0.0569 "	100.35 "	0.0554 "

The discrepancy of 6 millivolts between the *E.M.F.*'s of cells 3 and 4 at 0°, prepared with solutions having the same concentration in the two cases, is in marked contrast to the identity of the values at 25°, and has not yet been accounted for. As a rule, cells prepared with such solutions gave almost identical and steady values when kept at 25°.

In the following tables are given the constant *E.M.F.*'s of some cells as measured at 25°, and the corresponding values deduced for the transport number  $(1-n)$  for chloridion in anhydrous alcoholic hydrogen chloride. The values for  $(1-n)$  vary between 0.32 and 0.41 with cells prepared with acids having different concentrations, a variation which is probably not unreasonably large when the uncertainties in the calculation of boundary potentials are considered, and due regard is paid to the practical difficulties arising from the chemical instability of alcohol as contrasted with water.

The transport numbers were calculated by the usual equation:

$$E = 2n \frac{RT}{F} \log \frac{a_1 c_1}{a_2 c_2},$$

where  $E$  = electromotive force,

$n$  = transport number of the positive ion,

$R$  = the gas constant,

$T$  = absolute temperature,

$F$  = charge per gram-ion,

$c_1, c_2$  = concentrations of the electrolyte,

$a_1, a_2$  = degrees of dissociation in the two solutions.

If  $\lambda_1, \lambda_2$  are the molecular conductivities for concentrations  $c_1, c_2$  we have:

$$a_1/a_2 = \lambda_1/\lambda_2,$$

and, with the ordinary units:

$$E = 2n \times \frac{8.316 \times 298 \times 2.3026}{96540} \log_{10} \frac{\lambda_1 c_1}{\lambda_2 c_2} \text{ volts}$$

In one experiment:

$$E=0.0588; c_1=1.114n; c_2=0.102n;$$

$$\lambda_1=16.75; \lambda_2=33.8;$$

$$\therefore 2n = \frac{0.0588 \times 96540}{8.316 \times 298 \times 2.3026 \times \log_{10} \frac{1.114 \times 16.75}{0.102 \times 33.8}},$$

$$\therefore 2n = 1.3572,$$

$$\therefore 1-n=0.3214.$$

(1) *With Calomel Electrodes.*

$c_1$	$a_1$	$c_2$	$a_2$	$E$ (volt).	$1-n$
0.06408	0.550	0.00641	0.755	0.0602	0.41
1.114	0.255	0.1021	0.511	0.0564	0.35
1.114	0.255	0.1021	0.511	0.0593	0.32
0.7867	0.289	0.0731	0.545	0.0565	0.37
Mean.....					0.36

(2) *With Silver Electrodes.*

$c_1$	$a_1$	$c_2$	$a_2$	$E$ (volt).	$1-n$
0.7867	0.289	0.0731	0.545	0.0543	0.39
1.114	0.255	0.1021	0.511	0.0538	0.38
Mean.....					0.385

Mean of both series = 0.37.

Needless to say, perhaps, numerous results obtained before sufficient experience with such cells had been gained, or others in which definite constancy was not reached, are not included in the above list, but, even including these, the extreme of all values for  $(1-n)$  throughout lay between 0.28 and 0.47, and the value 0.37 may be regarded as the most probable one deduced from the whole of the experiments.

*Conductivities of Alcoholic Hydrogen Chloride.*

Some measurements of the conductivities of solutions of hydrogen chloride in alcohol at 25° have been carried out by Goldschmidt and Udby (*Zeitsch. Elektrochem.*, 1909, 15, 5) with the following results:

Concentration.	$\lambda_{25}$
0.1 <i>N</i>	34.1
0.05 <i>N</i>	39.0
0.025 <i>N</i>	44.7
0.0125 <i>N</i>	50.2
0.00625 <i>N</i>	55.6

The range of dilutions used by these observers is unfortunately

too narrow to allow of more than a very rough estimation of the limiting value of the conductivity at infinite dilution.

Baly, Burke, and Marsden (*Trans.*, 1909, **95**, 1100) have carried out measurements of the conductivity of alcoholic hydrogen chloride at 15°, from which they find the values 21.86 and 43.10 for the molecular conductivities at decinormal concentration and at infinite dilution respectively. From these numbers, however, it would appear possible that Völlmer's rule for the temperature-coefficient of salts, already referred to, cannot be extended to acids. Experiments to test this point are being made in this laboratory.

It was therefore thought desirable to redetermine the molecular conductivities at 25°, up to such dilutions that a limiting value could be found with some probability of accuracy. The results were, for the most part, identical with the numbers of Goldschmidt and Udby, except at the highest dilution, where somewhat lower values were obtained. The measurements were made by the Kohlrausch method in a small cell with platinised platinum electrodes which was almost completely filled with solution, and closed by a ground stopper. The admission of air causes a steady rise in conductivity, which is probably due to oxidation of the alcohol (compare Cohen, *Zeitsch. physikal. Chem.*, 1898, **25**, 1). With the above precautions, and frequent shaking of the cell, consistent numbers were finally obtained up to  $V=10^6$ .

Concentration.	$\lambda$ at 25°.	$\lambda$ from smoothed curve.
0.6341 <i>n</i>	20.42	20.24
0.06406 <i>n</i>	36.57	36.57
0.01282 <i>n</i>	45.56	47.00
0.00583 <i>n</i>	52.35	50.95
0.001025 <i>n</i>	57.00	57.00
[0.0000 <i>n</i>	—	66.5]

The value  $\lambda_{\infty}=66.5$  was obtained by Kohlrausch's method of extrapolation on the graph of  $\lambda$  against the cube-root of the concentration, which Philip and Courtman (*Trans.*, 1910, **97**, 1266) have shown to apply accurately to alcoholic solutions of tetramethylammonium iodide and potassium iodide.

#### Summary.

- (1) The electromotive forces of the concentration cells:
  - (a)  $\text{Hg}, \text{Hg}_2\text{Cl}_2, [\text{HClAlcohol}]_1, [[\text{HClAlcohol}]_2, \text{Hg}_2\text{Cl}_2, \text{Hg}.$
  - (b)  $\text{Ag}, \text{AgCl}, [\text{HClAlcohol}]_1, [[\text{HClAlcohol}]_2, \text{AgCl}, \text{Ag},$
 which appear to fulfil the conditions for reversibility, and as a rule give nearly constant values at 25°, have been studied.
- (2) The results indicate that the ratios of the mobilities of hydriions and chloridions are quite different in alcohol and in water.

the transport number of chloridion in alcohol being about 0.37, as contrasted with 0.16 in aqueous solution.

(3) It is shown that a number not very different from this is also indicated by a variety of other considerations.

(4) The transport numbers of most ions other than hydrion do not appear to be greatly affected by a similar change of solvent.

The work described in the present paper is being continued, and, in particular, examination is being made of the effect of change of temperature on cells of the kinds herein dealt with.

The influence of water on the potential of these cells is also under investigation, as it is hoped that in this direction evidence as to whether the chlorine ion unites with this substance may be forthcoming. Positive evidence in the case of the hydrogen ion has already been obtained in this laboratory by the use of the hydrogen electrode.

The authors' thanks are due to Mr. R. T. Hardman for valuable assistance during the course of the work, and they also desire to acknowledge their indebtedness to the Royal Society for a grant from the Government Grant Research Fund which defrayed much of the cost of the investigation.

SCHUNCK LABORATORY,  
THE UNIVERSITY, MANCHESTER.

# CLXI.—*Equilibrium in the System: Ethyl Alcohol, Acetic Acid, Ethyl Acetate and Water, and its Apparent Displacement by Hydrogen Chloride.*

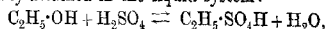
By WILLIAM JACOB JONES and ARTHUR LAPWORTH.

The equilibrium constant  $K = \frac{[H_2O][CH_3 \cdot CO_2 \cdot C_2H_5]}{[C_2H_5 \cdot OH][CH_3 \cdot CO_2 H]}$  is known to be approximately 4 for the homogeneous liquid system over a very wide range of temperature, its value being but slightly affected by the addition of small quantities of catalysts, by alterations in the relative amounts of the constituents, or by the use of various indifferent solvent media.

Whilst the activity of hydrogen chloride in alcohol is greatly diminished by small amounts of water, it is but imperceptibly affected by acetic acid or by ethyl acetate; hence, if the variations in the availability of hydrogen chloride are, in fact, due to com-

bination of the latter with water, then hydrogen chloride, when passed into an equilibrium mixture of water, ethyl acetate, alcohol, and acetic acid, should unite almost exclusively with the water when the latter is there in considerable quantity. The experience of Berthelot and Péan de Saint-Gilles with indifferent solvents would lead to the conclusion that the value of  $K$ , corrected for the quantities of the four constituents removed by the hydrogen chloride and rendered inert, would still remain nearly constant. The present paper describes measurements of this kind, which show that as the ratio of the amount of water existing in equilibrium to the amount of hydrogen chloride falls, the value of  $\psi$  (the apparent value of  $K$  calculated on the assumption that the water in the system is entirely in the free state) rises from 4 to 8 at least, indicating clearly that some of the water present combines with the hydrogen chloride. Further, assuming that this apparent variation in the "constant" is, as suggested, due to hydrate formation, it may be calculated that, roughly, two molecules of water associate with each molecule of hydrogen chloride present, although the existence of higher hydrates in a partly dissociated condition is not excluded.

Records of earlier work on somewhat similar lines exist; thus the state finally attained in the liquid system:



has recently been the subject of investigations by Zaitschek (*Zeitsch. physikal. Chem.*, 1897, **24**, 1) and by Kremann (*Monatsh.*, 1910, **31**, 245, 1031, 1051). Zaitschek found that at equilibrium

the quantity  $\frac{[C_2H_5 \cdot OH][H_2SO_4]}{[C_2H_5 \cdot SO_4H][H_2O]}$  varied greatly if the values for the

total concentration of water and sulphuric acid present were introduced. Assuming, however, that the sulphuric acid present was wholly in the form of the hydrate  $H_2SO_4 \cdot 2H_2O$ , a constant value for the above expression was obtained. On the other hand, Kremann found values  $1.7 \pm 0.2$  without making any allowance for the presence of hydrates, and concluded that the water in the form of hydrates is almost as effective a hydrolyst as is free water, and, further, that hydrated sulphuric acid combines with alcohol as readily as does the non-hydrated acid. In the light of what is now known of the behaviour of hydrogen chloride, however, Kremann's views appear most improbable, and the matter would seem to be more plausibly explained by assuming that at the fairly high temperatures he used the hydrates undergo more or less nearly complete thermal dissociation, for the basic affinity of water as compared with that of alcohol falls off very rapidly with rise in temperature. The case dealt with in the present paper is much

more simple in character, and the results appear capable of no other explanation than that the hydrogen chloride removes water preferentially from the system water, alcohol, acetic acid, and ethyl acetate.

It is of interest to note that Berthelot and Péan de Saint-Gilles (*Ann. Chim. Phys.*, 1863, [iii], 68, 225) record an experiment showing that the presence of barium chloride affects to a marked extent the proportion of benzoic ester hydrolysed by water at 200°, and add: "Peut-être l'affinité du chlorure de barium pour l'eau concourt-elle à affaiblir l'action décomposante de cette dernière substance" (*loc. cit.*, p. 248).

#### EXPERIMENTAL.

The procedure in each of the experiments was as follows. Ordinary test-tubes were subjected to the action of a current of steam, dried, constricted near the open end, and weighed. By means of narrow thistle-funnels passed through the constriction in the test-tube, quantities of ethyl acetate and hydrochloric acid were introduced. The tube was weighed after each such addition, and then sealed off at the constriction, when it was immersed in a bath, kept at  $25^{\circ} \pm 0.02^{\circ}$ , and frequently shaken. The mixture became homogeneous after about one to two hours when 7.268*N*-hydrochloric acid was used, and the tubes were broken and their contents analysed after forty to fifty-eight hours; in experiments Nos. 1 and 4, however, thirty-five days elapsed before they were removed from the bath. When 0.1185*N*-hydrochloric acid was employed, complete admixture did not occur until after nearly three weeks, and in such cases the tubes were not removed before thirty-six days. The dried tubes were finally broken in excess of carefully neutralised sodium acetate solution, which was then diluted to a litre, portions of 100 c.c. being taken and titrated against standard baryta solution, with phenolphthalein as indicator. The amount of hydrogen chloride which remained was checked by means of standard silver nitrate. The diluting water, sodium acetate solution, and nitric acid were tested, and found to be free from chloride. Kahlbaum's purest ethyl acetate was used throughout, and the baryta solutions used for titration were frequently standardised against a 0.1185*N*-hydrochloric acid solution which had been analysed gravimetrically. The 7.268*N*-hydrochloric acid solution was standardised immediately before each measurement. All the measuring vessels used were either standard or had been calibrated. The results of the experiments are summarised in the table.

In line *A* are given the numbers of the experiments.

" " *B* " " weights of ethyl acetate taken.



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In line *C* are given the weights of 7·268*N*-hydrochloric acid.  
 " " *D* " " weights of 0·1185*N*-hydrochloric acid.  
 " " *E* " " amounts of hydrogen chloride taken in  
 gram-molecules.  
 " " *F* " " amounts of hydrogen chloride found at  
 the end of the experiment.  
 " " *G* " " total titres (acetic acid plus hydrogen  
 chloride) in c.c. of normal acid.

In lines *H*, *K*, and *L* are given the total apparent number of  
 gram-molecules of acetic acid (and alcohol), of water, and of ester,  
 respectively, found at equilibrium.

In line *R* are given the ratios  $[H_2O(\text{total})]/[HCl]$  in each case.

" " *S* " " values of  $\psi$ .

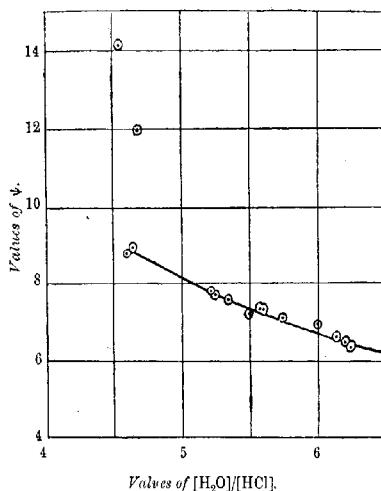
$$\psi = \frac{[H_2O(\text{total})][CH_3 \cdot CO_2 \cdot C_2H_5]}{[CH_3 \cdot CO_2H][C_2H_5 \cdot OH]}$$

Two other experiments were carried out, giving  $\psi = 14\cdot19$  and  
 11·98 respectively; there was doubtless in both these cases some slip  
 in the initial weighings. The apparent value,  $\psi = 4\cdot35$ , experiment  
 No. 14, corresponds with the formation of 0·6761 gram-molecule  
 of ethyl acetate and of water from 1 gram-molecule of acetic acid  
 and of ethyl acetate. Berthelot and Péan de Saint-Gilles (*loc. cit.*)  
 found that, at 9°, 1 gram-molecule of ethyl alcohol and of acetic  
 acid combined to form 0·665 gram-molecule of ethyl acetate and  
 of water, in the absence of hydrogen chloride ( $[H_2O]/[HCl] =$   
 infinity).

The diagram shows the variation in the value of  $\psi$ , the apparent  
 value of the equilibrium constant with variation in the value of  
 the ratio  $[H_2O(\text{total})]/[HCl]$ , where the square brackets refer to  
 relative molecular concentration at equilibrium. The two very  
 doubtful results obtained are included, although having regard to  
 their quite anomalous position on the diagram, it would probably  
 have been legitimate to discard them.

<i>A</i> ...	1.	2.	3.	4.	5.	6.	7.	8.
<i>B</i> ...	12·3121	11·7921	11·3334	10·4887	11·1817	8·0458	7·0384	10·1819
<i>C</i> ...	2·0154	1·9992	3·2524	3·9337	4·6554	6·1489	4·2332	6·4593
<i>D</i> ...								
<i>E</i> ...	0·01272	0·01265	0·02494	0·02482	0·02238	0·03880	0·02671	0·04076
<i>F</i> ...	0·0129	0·01264	0·0255	0·0255	0·0300	0·0397	0·0273	0·0419
<i>G</i> ...	40·04	39·30	63·68	62·95	71·27	78·81	58·20	87·32
<i>H</i> ...	0·02732	0·02665	0·03874	0·03723	0·04189	0·04001	0·03149	0·04656
<i>K</i> ...	0·05863	0·05884	0·1303	0·1306	0·1571	0·2230	0·1491	0·2295
<i>L</i> ...	0·1125	0·1073	0·0900	0·0820	0·0851	0·05142	0·04849	0·0690
<i>R</i> ...	4·61	4·65	5·22	5·26	5·35	5·75	5·58	5·63
$\psi$ .....	8·83	8·90	7·81	7·73	7·62	7·17	7·29	7·80

	9.	10.	11.	12.	13.	14.	15.
A ...	7.4224	5.811	5.3922	5.6624	3.9716	11.5222	11.0326
B ...	5.8523	7.6946	9.3930	11.0293	8.6004	—	—
C ...	—	—	—	—	—	4.4614	6.0886
D ...	0.03693	0.04855	0.05928	0.06958	0.05423	0.000528	0.000720
E ...	0.0371	0.0490	0.0610	0.0706	0.0542	—	—
F ...	74.42	84.35	96.02	109.8	83.43	57.38	68.04
G ...	0.03749	0.03580	0.03676	0.0402	0.02917	0.05685	0.06232
H ...	0.2127	0.2933	0.3648	0.4316	0.3386	0.1898	0.2744
I ...	0.04684	0.03032	0.02452	0.02414	0.01596	0.0741	0.06804
J ...	5.76	6.04	6.16	6.20	6.24	359.7	381.0
K ...	7.09	6.94	6.62	6.45	6.35	4.35	4.45



Experiments with solutions, 1.000 gram of which contained 0.000132 gram-molecule of hydrogen chloride and 0.0068 gram-molecule of calcium chloride, were also begun, but it was found that they did not become homogeneous, even after six months, or when subsequently heated at 100° for twenty hours.

#### Summary.

(1) Measurements have been made of the total quantities of alcohol, acetic acid, ethyl acetate, and water at equilibrium in presence of varying proportions of hydrogen chloride.

(2) No appreciable amount of ethyl chloride is formed under the conditions of the experiments.

(3) The apparent value for the equilibrium constant varies from 4 to over 8, as the concentration of the hydrogen chloride increases.

(4) The apparent diminution in the active mass of the water corresponds nearly with the formation of a compound having the formula  $\text{HCl} \cdot 2\text{H}_2\text{O}$ , or of compounds having that mean composition.

It is intended to use the above methods in certain other cases, and especially to examine the influence of some salts on the value of the equilibrium constant in systems containing water.

The authors desire to state that the expenses of this investigation were partly defrayed by a grant from the Government Grant Research Fund of the Royal Society, for which their thanks are due.

CHEMICAL LABORATORIES.  
UNIVERSITY OF MANCHESTER.

## CLXII.—*The Purification and Properties of Acetic Acid.*

By WILLIAM ROBERT BOUSFIELD, M.A., K.C., and  
THOMAS MARTIN LOWRY, D.Sc.

ON account of its convenient melting point, boiling point, and other physical properties, acetic acid has been used extensively as a material for physico-chemical investigations, such as those of Oudemans on the density of solutions (*Zeitsch. Chem.*, 1866, 2, 150), of Ramsay and Young on vapour pressures (*Phil. Trans.*, 1884, 175, 469) and on vapour densities (*Trans.*, 1886, 49, 790), and of de Visser on the influence of pressure on melting point (*Rec. trav. chim.*, 1893, 12, 101).

It has frequently been assumed that a pure acid can be obtained merely by freezing the liquid and pouring away the unfrozen mother liquor from which the crystals have separated. In recent years this assumption has been proved to be false, and it has become a matter of some importance to obtain a more efficient method of purifying the acid, and to redetermine several of its physical constants by measuring the properties of the purified material. It is, indeed, remarkable that in spite of its extensive use in cryoscopy, doubt should still exist as to the true freezing point of the acid; still greater uncertainty is found in the case of other physical properties, and the conductivity data appear to be entirely untrustworthy.

*Maximum Acetic Acid as a Standard of Electrolytic Conductivity.*

Our attention was first directed to the problem nearly ten years ago, when an attempt was made to utilise the acid as a standard of electrolytic conductivity. The electrolytes usually employed for calibration include not only solutions made up to a measured concentration, such as 21 per cent. *N*-, *N*/10-, *N*/50-, and *N*/100-solutions of potassium chloride, but also saturated solutions, such as those of salt and gypsum, and solutions having a maximum conductivity, such as those of sulphuric acid, magnesium sulphate, and acetic acid. The saturated solutions cannot be regarded as very satisfactory, on account of their slowness in recovering from changes of concentration consequent upon exposure to variable atmospheric temperatures; but solutions of maximum conductivity are very convenient to use, as their conductivity is not appreciably affected by small errors in concentration. Two of these solutions,

Sulphuric acid.....	30 per cent.	$\kappa_{18}=0.7398$ mho.
Magnesium sulphate .....	17.4 per cent.	$\kappa_{18}=0.4922$ mho.

are in constant use, but the third,

Acetic acid .....	16 per cent.	$\kappa_{18}=0.0016$ mho.,
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proposed by Kohlrausch in 1876, has been abandoned as untrustworthy, in spite of the great convenience that would attend its use in the calibration of vessels of small resistance capacity.

The reason for this abandonment was at once clear when we attempted to use the acid for calibration, taking for its maximum conductivity the value  $\kappa_{18}=0.001619$  given in Kohlrausch and Holborn's "*Leitvermögen der Elektrolyte*," p. 155. In the case of one particular vessel, the values obtained for the resistance capacity were as follows:

KCl 21 per cent. 1.989.	KCl <i>N</i> /10 1.968.	NaCl (saturated) 1.971.
KCl <i>N</i> 1.971.	KCl <i>N</i> /100 1.969.	Acetic acid 1.944.

The last observation, unless due to some unsuspected error, showed that the conductivity of the acid was considerably higher than had previously been supposed, namely 1640 gemmho, instead of 1619. A second sample of acid which had been frozen and drained behaved in the same way, giving a maximum conductivity of 1645 gemmho. As these values differed so seriously from those hitherto accepted as correct, a systematic investigation was undertaken in order to ascertain the source of the discrepancy, as well as the true value for the maximum conductivity of the acid. In this investigation we had the advantage of using a far more delicate test of the purity of the acid than those which had been employed

previously, since the course of the purification could be followed with ease and certainty by measuring the maximum conductivity of the different samples.

*Fractional Distillation of Acetic Acid.*

Fractional distillation showed at once the presence of substances of high boiling point and low conductivity and of low boiling point and high conductivity. An attempt was therefore made to fractionate a pure acid from a large sample of about 10 litres. The first distillation gave eight fractions, ranging in maximum conductivity from 1833 to 1655 gemmho. When redistilled with a 12-pear still-head, the first portion ( $\kappa$  1833) gave fractions ranging in maximum conductivity from 2030 to 1638 gemmho, whilst the last portion ( $\kappa$  1655) gave fractions ranging from 1714 to 1560 gemmho. The last fraction ( $\kappa$  1560), when redistilled, gave portions of maximum conductivity 1644, 1624, 1600, and 1500, leaving behind a residue of about 10 grams having the disagreeable odour of the higher fatty acids.

Fractional distillation had thus resolved the acid into portions ranging in maximum conductivity from 1500 to over 2000 gemmho, but at no point was there any evidence of a steady value being reached, every portion examined being found to be resolvable even after repeated distillation into fractions of different conductivity.

*Purification by Freezing.*

Whilst the fractional distillation of the acid was in progress, attempts were made to separate a pure acid by freezing. Two of the intermediate fractions were selected and allowed to crystallise; the mother liquor was poured off from the crystals, and both were diluted to 16 per cent. in order to measure their maximum conductivity. The maximum conductivity values obtained were as follows:

Mixture of fractions from 1625—1650.

Frozen out.....	1636
Unfrozen .....	1636.

Mixture of fractions from 1650—1675.

Frozen out.....	1652
Unfrozen .....	1652.

The conductivity of the acid was therefore not affected by fractional freezing, and this method could not be used to prepare a pure acid of definite conductivity. A preliminary freezing is, however, of considerable value in reducing the quantity of impurities to be dealt with by the more efficient methods of purification which are described below.

### Purification by Oxidation.

From its behaviour on fractional distillation, it seemed probable that the crude acid might be a mixture of:

	Max. cond.	B. p.
Formic acid .....	10380	101°
Acetic acid .....	1640	118
Propionic acid.....	1113	141
Butyric acid .....	986	163

and perhaps other acids of higher molecular weight. On account of its high conductivity, formic acid would be by far the most dangerous impurity, and attempts were therefore made to get rid of it by chemical methods. The low-boiling fraction of maximum conductivity 1987 was distilled from potassium dichromate with the idea of removing the formic acid by oxidation, but the distillate still gave the high value 1923, and was evidently far from pure. A second attempt was made to remove the formic acid by distilling from sodium, in the hope that the stronger acid might thus be retained; this method was also a failure, the distillate having a maximum conductivity 1957. Success was finally achieved by the use of potassium permanganate, which reduced the maximum conductivity of a sample from 1753 to 1644 by a single distillation.

Further tests showed that by the use of potassium permanganate an acid of definite properties could be obtained without difficulty from any of the crude commercial samples. In the table which follows, *C* refers to a commercial acid which had been frozen out and drained in order to remove a part of the water, as well as a certain proportion of impurities of high and low boiling points. The acids *A* and *B* were derived from the fractional distillation described above; it should be noted that the original acid was an exceptionally bad sample and had not been subjected to any preliminary purification by freezing; the portions *A* and *B* were almost the extreme fractions, and contained in a concentrated form the impurities of high- and of low-boiling point present in the 10 litres of acid used for the fractionation; they therefore provided a very extreme test of the methods which we have devised for purifying the acid. The course of the purification is shown in the following table:

	<i>A</i> .	<i>B</i> .	<i>C</i> .
Initial maximum conductivity	1650	1780	1646
Acid distilled from permanganate with 12-pear still-head:			
First portion .....	1646	1808*	1640
Second portion .....	1643	1640	1639
Third portion.....	1623	1638	1640
Fourth portion .....	—	—	1639

\* More permanganate added after this portion had been collected.

Redistilled from a few grams more permanganate:

	A.	B.
First portion .....	*1638 (60 c.c.)	*1639 (50 c.c.)
Second portion .....	1637 (1000 c.c.)	1639 (1000 c.c.)
Third portion.....	1638 (1000 c.c.)	1637 (1000 c.c.)
Fourth portion .....	*1630 (150 c.c.)	*1637 (60 c.c.)

Redistilled from a few crystals of permanganate:

First portion .....	*1637 (120 c.c.)	1640 (200 c.c.)
Second portion .....	1641 (1000 c.c.)	1640 (750 c.c.)
Third portion.....	1638 (750 c.c.)	1639 (750 c.c.)
Fourth portion .....	*1630 (80 c.c. to dryness)	

Again distilled:

First portion .....	1640 (500 c.c.)	—
Second portion .....	1640 (500 c.c.)	—
Third portion .....	1639 (500 c.c.)	—

\* Rejected on subsequent distillation.

It will be seen from the above table that a single distillation from permanganate with a 12-pear still-head was sufficient to produce an acid of definite properties, except in the case of a sample in which impurities of higher boiling point had been accumulated deliberately. Even here the quantity of high-boiling impurities was only sufficient to lower the conductivity of the acid by one or two parts in a thousand, but three distillations were required before the final fraction of acid was found to give a normal conductivity maximum. In the case of the acid in which impurities of lower boiling point had been accumulated, the only modification required was to add a rather larger quantity of permanganate in order to secure their complete oxidation.

It should be noticed that the values given above for the maximum conductivity are only relative; the true value of the maximum conductivity is discussed in a later section.

#### *The Freezing Point of Acetic Acid.*

The acid, purified as described above, still contains water, which can be removed by freezing and draining. This operation was carried out on a relatively large scale in order to avoid any lowering of the freezing point consequent on the hygroscopic character of the acid. Two Winchester quarts of the purified acid were used, and when sufficiently reduced in bulk were poured into a single bottle and again frozen repeatedly; the quantity remaining for the final determination of the freezing point was not less than 1500 c.c. A device of some value, especially in the later stages of the fractionation, consists in allowing a small lump of the solid acid to remain unmelted as a nucleus for the further freezing of the acid; glaciation then proceeds smoothly over the sides of the

bottle, the thickness of the coating increasing steadily until only a small cone of liquid acid remains in the centre; when the proportion of water is small, the frozen acid is perfectly transparent and compact, and the quantity of water mechanically retained is very much smaller than when freezing is started by shaking the bottle or by introducing a crystal into the cold acid. The freezing point of the liquid acid can be determined at any stage of the freezing by breaking through the crust of acid and lowering a thermometer into the central cone of liquid.

The following table shows the results of successive freezings of the purified acid:

Initial F.P. ...	16.31°	16.45	16.55	16.58	16.59	16.595	16.60
Final F.P. ....	15.98	16.07	—	16.49	16.49	16.54	16.56

The quantity of acid remaining unfrozen when the "final freezing point" was taken varied from 100 to 200 c.c. in the case of the first five freezings. For the last two freezings the volume of unfrozen acid was only about 20 c.c. from an initial volume of 1500 c.c. In the last freezing the difference between the initial and final freezing points was only 0.04°.

Since each 0.1 per cent. of water lowers the freezing point by 0.2014° (de Visser, *loc. cit.*, p. 118), the amount of water remaining in our acid would be 0.02 per cent. on 20 c.c., or 0.0003 per cent. on the total bulk of 1500 c.c.; the corresponding error in the freezing point would be about 0.0005°. The thermometer used was standardised from one which had been calibrated at the Reichsanstalt, and more recently with very great care at the National Physical Laboratory, the readings of which could be relied on within 0.005°; we consider that our determination of the freezing point of acetic acid is correct within the same limits at  $16.60 \pm 0.005^\circ$ .

In this view we are confirmed by the fact that our value is in agreement with the figure  $16.5965^\circ$  ( $dt/dp=0.02435$ ) given by de Visser (*loc. cit.*) in his investigation of the influence of pressure on freezing point. In these experiments 10 kilos. of acid were frozen fractionally during a period of seven months, until the difference of freezing point between the acid and mother liquor did not exceed 0.0004° when only 1/80 of the acid remained unfrozen. These experiments on the freezing point of acetic acid are obviously by far the most accurate that have been made; the lower values given by almost all other observers are to be attributed to imperfect purification; occasional higher values, for example, 16.7° or 17°, appear to be only rough approximations.



*The Boiling Point of Acetic Acid.*

The boiling point of the purified acid was determined with the help of a thermometer graduated in tenths of a degree on an open scale from  $75^{\circ}$  to  $125^{\circ}$ . The thermometer had been standardised recently at the National Physical Laboratory, the corrections being given to  $0.01^{\circ}$  at intervals of  $5^{\circ}$ . In order to reduce the correction for exposed stem, the flask containing the acid was provided with a still-head 40 cm. long, and the thermometer was arranged so that the mercury thread rose only just above the level of the cork. Two hundred c.c. of acid were used, and it was found that three-quarters of this quantity distilled between  $118.10^{\circ}$  and  $118.12^{\circ}$  under 768.2 mm. pressure, after applying a correction of  $-0.05^{\circ}$  for thermometer error and  $+0.04^{\circ}$  for exposed stem. The barometer height reduced to  $0^{\circ}$  and  $45^{\circ}$  latitude was 766.0 mm., and the correction to be applied to the boiling point may be taken as  $0.038^{\circ}$  per mm. (Ramsay and Young, *Trans.*, 1886, **49**, 806, give  $0.032^{\circ}$ ; Schmidt, *Zeitsch. physikal. Chem.*, 1891, **7**, 433, gives  $0.043^{\circ}$ ; Kahlbaum, *Zeitsch. physikal. Chem.*, 1898, **26**, 577, gives  $0.038^{\circ}$ ). The corrected boiling point of the acid may therefore be taken as  $118.11^{\circ} \pm 0.02^{\circ}$  under 766 mm. (corr.) and  $117.88^{\circ} \pm 0.05^{\circ}$  under 760 mm. (corr.) pressure. The substantial accuracy of these observations and of the corrections applied in reducing the boiling point is shown by the fact that two preliminary observations under 750 mm. pressure, in which the stem correction was nearly half a degree, gave values for the corrected boiling point which were within  $0.02^{\circ}$  of that recorded above.

Our value for the boiling point is considerably below those hitherto accepted, practically all of which have been above  $118^{\circ}$ . In particular it may be noted that Ramsay and Young (*loc. cit.*) give the value  $118.5^{\circ}$ , Schmidt (*loc. cit.*) gives the value  $119.2^{\circ}$ , and Kahlbaum (*loc. cit.*) the value  $118.6^{\circ}$ . The conclusion may therefore be drawn that the last traces of impurity which are removed by the methods we have adopted are substances which have the normal effect of raising the boiling point, as well as lowering the freezing point, of the acid. It should be noticed, however, that the boiling point soon falls below the normal value if the acid is allowed to absorb water; a low boiling point is therefore not a trustworthy indication of the purity of the acid.

*The Density of Acetic Acid.*

The density of the acid was determined in a double pycnometer of the type recently described by one of us (Bousfield, Trans., 1908, 93, 679). The figures obtained were:

$$\begin{array}{l} d_{18^{\circ}/4^{\circ}} = 1.05148 \\ d_{20^{\circ}/4^{\circ}} = 1.04922 \end{array} \left. \begin{array}{l} \\ \end{array} \right\} \text{difference for } 1^{\circ} = 0.00123.$$

Our experience with this pycnometer justifies us in regarding these results as correct within a single unit in the last figure.

With the help of the temperature-coefficient given above, it is possible to compare our value at  $18^{\circ}$  with those of other observers, as follows:

	<i>t</i> .	<i>d</i> .	<i>d</i> $18^{\circ}/4^{\circ}$ .	Diff.
Oudemans (1866) .....	$15^{\circ}/4^{\circ}$	1.0553	1.0516	+0.0001
Perkin (1884) .....	$15^{\circ}/15^{\circ}$	1.0568	1.0530	+0.0015
" " .....	$15^{\circ}/15^{\circ}$	1.05704	1.0532	+0.0017
Ramsay (1886) .....	$20^{\circ}/4^{\circ}$	1.0491	1.0516	+0.0001
de Visser (1893) .....	$16.6^{\circ}/4^{\circ}$	1.05315	1.05143	-0.00065
Jones (1894) .....	$16.5^{\circ}/4^{\circ}$	1.0534	1.0516	+0.0001

It will be seen that our value is, as in the case of the freezing point, in very close agreement with that of de Visser; the difference, amounting only to 0.00005, is perhaps due to the increased accuracy which we have secured by the use of a large pycnometer of special design, and not to any difference in the quality of the acid. Three observers using acetic acid purified in the ordinary way have given the density as 1.0516, a value that exceeds ours by one unit in the fourth decimal place, and must be attributed to the same impurities which gave rise to the lower freezing points,  $16.4^{\circ}$  to  $16.5^{\circ}$ , recorded by these authors. The chemical methods of purification adopted by Perkin have raised his values for the density by more than 0.001, and must have given an impure product, containing, possibly, appreciable quantities of acetic anhydride.

*The Maximum Conductivity of Acetic Acid.*

In order to determine the maximum conductivity of the acid, a vessel was calibrated by means of standard solutions of potassium chloride, using the values for the conductivity given by Kohlrausch and Holborn ("Leitvermögen der Elektrolyte," p. 204), namely:

$$\begin{array}{ll} \text{KCl } N/50. & \kappa_{18} = 0.002397. \\ \text{KCl } N/100. & \kappa_{18} = 0.001225. \end{array}$$

These solutions were prepared by diluting to a known volume weighed quantities of a normal solution prepared by dissolving 74.59 grams of potassium chloride to 1044.92 grams of solution, according to the directions given by Kohlrausch, and not according to the more recent values for the equivalent of the salt. The

salt had been crystallised several times from conductivity water until it showed no trace of sodium in the flame test. The water used had a conductivity of  $1.5 \times 10^{-6}$ , which was added to the above values.

The values deduced for the capacity of the vessel were:

From KCl N/50.  $C=0.2466_1$   
From KCl N/100.  $C=0.2466_2$ .

This gave for the maximum conductivity of the acid the figure:

$$\kappa_{18} = 0.001841_3 + 0.0000298 (t - 18),$$

the temperature-coefficient being deduced from a series of observations in the neighbourhood of  $18^\circ$ .

In determining the maximum conductivity, the Kohlrausch "wheel-bridge" was used, with an alternating current and telephone. The conductivity vessel contained about 40 c.c. Ten c.c. of acid were diluted in a beaker with about 40 c.c. of water from a burette; the conductivity was measured, and the observations were repeated after each of a series of successive dilutions. Thus, in the following series of observations, a minimum bridge-reading and a maximum

Water added .....	44	46	48	50	51	52	54	57 c.c.
Bridge-reading.....	601.9	601.6	601.1	601.0	601.0	601.0	601.1	601.6

conductivity were reached when 10 c.c. of acetic acid were diluted with 51 c.c. of water; the bridge-reading 601.0, after making the necessary corrections, gives the value for the maximum conductivity set out above.

#### *Practical Methods of Purification.*

Having found a method by which acetic acid of the highest degree of purity may be prepared, and having established a reliable value for the maximum conductivity of the acid, it was of interest to determine what amount of purification is needed to produce an acid which can be relied on to give a correct value for this maximum. After testing a number of acids we are able to state that a commercial acid, when purified by freezing and pouring off the liquid portion in order to reduce the amount of water and of oxidisable material, can be relied on to give a correct value if distilled slowly from 2 per cent. of its weight of permanganate, using a 12-pear still-head to retain acids of higher boiling point. In practice the acid can be evaporated to quite a small bulk, but if a standard acid is required it is convenient to reject the first 25 per cent., which contains an excessive proportion of water, and also the last 25 per cent., which may contain homologous acids. The following tests on three of Kahlbaum's acids may be regarded as typical of the observations made.

A. *Kahlbaum's Acid*, "100 per cent."—About one-third of the

acid was melted and poured off; this gave a maximum conductivity 1643 gemmho, and is therefore nearly pure, but cannot be used as a standard without purification.

B. *Kahlbaum's Acid "Free from Higher Homologues."*—The original sample, after pouring away about one-quarter from the partly frozen acid, also gave a maximum conductivity 1643 gemmho. The last 150 c.c. from the distillation of 1500 c.c. of this acid (using a still-head and 1 per cent. of permanganate) gave a normal maximum 1641 gemmho; the whole of the acid could therefore be used as a standard after distillation.

C. *Kahlbaum's Acid, 99—100 per cent.*—About one-third was poured away from the partly frozen acid; 2 per cent. of permanganate was added, and the acid was distilled through a 12-pear still-head until only a small residue (containing manganese acetate) was left. The first and last fractions showed a normal conductivity 1641 gemmho, and the whole of the distillate was therefore available for standard acid.

From the above observations, as well as from those quoted earlier in the paper, it is clear that a pure acid can be prepared very readily with the help of potassium permanganate. The original acids usually contain oxidisable material, which raises the maximum conductivity, but this is easily removed by the methods now described. Acids of higher boiling point do not produce any marked error in the maximum conductivity unless (as in our fraction "A") they are present in altogether abnormal quantities; with a 12-pear still-head the acid can be boiled almost to dryness without spoiling the acid for use as a standard of conductivity.

Orton has recently shown that an acetic acid, which is resistant to bromine and which does not give the Adamkiewicz reaction, can be prepared by distilling the commercial acid from phosphoric oxide—one of the two methods used by Perkin in 1884 to purify the acid from moisture. Although this method of treatment is liable to give rise to an acid of lower freezing point and higher density, we have found a normal value, 1642 gemmho, for the maximum conductivity of a specimen kindly sent to us by Professor Orton. We are also indebted to him for the information that a specimen of our acid, which had been prepared in 1902, and might therefore have deteriorated by keeping (it has been suggested that acetic acid oxidises spontaneously to glyoxylic acid), was resistant to bromine, and did not give the Adamkiewicz reaction.

ST. SWITHINS,  
HENDON, N.W.

130, HORSEFERRY ROAD,  
WESTMINSTER, S.W.

CLXIII.—*Some Oxidation Products of the Hydroxybenzoic Acids. Part III.*

By ARTHUR GEORGE PERKIN.

DURING some experiments with flavellagic acid it was noted that when this substance is heated with sulphuric acid to a high temperature it is converted into a new colouring matter (Proc., 1906, 22, 114). The investigation of this forms the subject of the present paper.

In a preliminary trial 3.65 grams of flavellagic acid suspended in 30 c.c. of 100 per cent. sulphuric acid were heated rapidly on the sand-bath to 230°, causing the formation of a red-coloured liquid, which effervesced briskly owing to the evolution of sulphur dioxide. The flame was now lowered so that in about half an hour the temperature had fallen to 190°, when the heating was discontinued, the mixture allowed to cool, and poured into a large volume of water. A dull green-coloured precipitate was thus produced, and this was collected, washed, and dried, yielding an almost black, resinous mass, which did not appear to be susceptible of purification by the usual methods. In the finely powdered condition it was therefore added to an excess of hot acetic anhydride containing a little sulphuric acid, and on heating to boiling the dark brown solution gradually deposited a yellow, crystalline powder. This was collected, washed with acetic anhydride, and crystallised from nitrobenzene, from which it separated in pale yellow needles, melting at about 324–329°, and very sparingly soluble in the usual solvents. The yield was 1.2 grams:

Found: C=53.12; H=3.34.

$C_{14}O_{10}(C_2H_3O)_6$  requires C=53.22; H=3.07 per cent.

The acetyl compound suspended in boiling acetic acid was hydrolysed with sulphuric acid in the usual manner, and the product crystallised from pyridine, the only satisfactory solvent for this purpose. An analysis of the substance dried at 160° gave the following result:

Found: C=50.09; H=2.08.

$C_{14}H_6O_{10}$  requires C=50.29; H=1.79 per cent.

The compound consists of small, pale yellow, prismatic needles, which melt above 360°, and are very sparingly soluble in the usual solvents. Concentrated solutions of the alkali hydroxides dissolve it with a greenish-yellow colour, which on dilution become green, and finally of a beautiful blue colour, and these changes

appear to arise from oxidation. If to the substance suspended in water dilute alkali is added drop by drop, the blue coloration is immediately produced, and is of a fairly permanent character. Sodium and potassium carbonate solutions also give blue liquids. As in general properties this new compound closely resembles both ellagic and flavellagic acids, the name *caeruleoellagic acid* is proposed for it. It was now interesting to determine if ellagic acid when heated with sulphuric acid under these conditions reacts in a similar manner, and experiment indicated that this was the case. The crude product thus obtained yielded an acetyl compound, melting at 325—329°, and was identical with acetylcaeruleoellagic acid:

Found: C=53.18; H=3.32.

$C_{14}O_{10}(C_2H_2O)_6$  requires C=53.22; H=3.07 per cent.

An acetyl determination by the indirect method gave 57.24 per cent. of caeruleoellagic acid dried at 160°, whereas the quantity required by the above formula is 57.00 per cent.

The colouring matter thus obtained was analysed with the following result:

Found: C=50.21, 50.01; H=2.44, 2.17.

$C_{14}H_6O_{10}$  requires C=50.29; H=1.79 per cent.

Experiments were now carried out with the object of preparing larger quantities of caeruleoellagic acid, and for this purpose flavellagic acid was employed, as this can be more economically prepared from gallic acid than ellagic acid itself.

The results were at first disappointing, for under the conditions given above and employing mixtures of 20 grams of flavellagic acid in 200 c.c. of sulphuric acid (100 per cent.), it was not easy to control the reaction, and the yield, which in the best circumstances was of a poor character, was thereby considerably diminished. It became evident as the result of numerous trials that caeruleoellagic acid, or possibly the sulphuric ester at first produced, undergoes further change in the presence of sulphuric acid more or less rapidly between 190° and 230°, with formation of a bright yellow compound, and in this case the bright red colour of the acid liquid gradually assumes a dull brown tint. On the other hand, by digesting for a very short time, unattacked flavellagic acid is likely to be present in the final product, the complete elimination of which is exceedingly troublesome. Ultimately it was discovered that the most satisfactory results were obtained by heating the acid mixture to 200°, and at once allowing the temperature to fall to 190°, and remain so for thirty minutes, or by heating to 185° for three-quarters of an hour. The product on pouring into

water was at first dark coloured, but on keeping or boiling the mixture became yellow, suggesting that a sulphuric ester of caeruleoellagic acid or of some accompanying impurity was at first present. Again, if the original red sulphuric acid solution was treated with cold acetic acid a dull red precipitate separated, which in contact with water gradually assumed a yellow tint.

The yield of crude colouring matter, which, when dry, consisted of a dull yellow powder, was, when prepared at the lower temperature, approximately equal to 100 per cent. by weight of the flavellagic acid employed, and from this about 57 per cent. of the pure acetyl derivative could be produced. It was incidentally noted that acetylcaeruleoellagic acid is in reality colourless, and not pale yellow as previously stated, although the latter tint is remarkably persistent and not easily removed. After repeated purification it melted and decomposed at 330—332°, sintering somewhat earlier.

By treatment with fuming sulphuric acid (70 per cent.) at 45—50°, a method which is employed for the preparation of higher hydroxylated compounds in the anthraquinone group of colouring matters, flavellagic acid remains intact, and again it was observed in the high temperature experiments described above that the use of boric acid is not beneficial.

*Benzoylcaeruleoellagic acid* is prepared by heating caeruleoellagic acid with excess of benzoic anhydride to 220—230° until a clear solution is produced, the reaction being much facilitated by the addition of two or three drops of pyridine, and subsequently at 190—200° for two hours. On cooling to 170—180° and stirring, a semi-solid, crystalline mass is produced, and this sparing solubility of the benzoyl compound in hot benzoic anhydride is characteristic of caeruleoellagic and ellagic acids, and distinguishes these compounds from flavellagic acid, which yields a much more readily soluble benzoyl derivative. To the mixture while still warm a little hot alcohol was added, the colourless powder collected, and purified by recrystallisation from a mixture of nitrobenzene and alcohol. It melted at 343—345°:

Found: C=70.13; H=3.25.

$C_{14}O_{10}(C_7H_5O)_6$  requires C=70.14; H=3.13 per cent.

A benzoyl determination was carried out by suspending the substance (1.15 grams) in a mixture of acetic acid (45 c.c.) and sulphuric acid (14 c.c.), and boiling for about fifteen minutes. The caeruleoellagic acid was collected, and dried at 160°:

Found:  $C_{14}H_8O_{10}$ =35.28.

$C_{14}O_{10}(C_7H_5O)_6$  requires  $C_{14}H_8O_{10}$ =34.86 per cent.

*Oxidation of Ellagic and Flavellagic Acids with Arsenic Acid.*

As caeruleoellagic acid was presumably formed by the introduction of an hydroxyl into flavellagic acid, and of two such groups into ellagic acid, it was sought to determine if the same result would be effected by the oxidation of these colouring matters in sulphuric acid solution with arsenic acid. It is well known, for instance, that under similar conditions alizarin gives purpurin, and other cases could be cited.

Twenty grams of flavellagic acid in 200 c.c. of 96 per cent. sulphuric acid at 100° was treated with 20 grams of arsenic acid, causing the gradual production of a greenish-black precipitate, evidently an arsenic compound of flavellagic acid, in such quantity that the mixture became semi-solid. At the same time, carbon dioxide commenced to be evolved in quantity, and this continued until the precipitate had disappeared, and a rich brown-coloured liquid had been produced. The solution was now heated to 130° for two hours, poured into water, the mixture boiled, the precipitate collected, and repeatedly washed. The product when dry consisted of a brown powder, which weighed 13.5 grams, and was soluble in dilute alkali with a blue coloration. With acetic anhydride and sulphuric acid this gave a colourless, crystalline acetyl derivative (15 grams), but this was evidently a mixture, and attempts to recrystallise it from hot nitrobenzene resulted in the formation of a gelatinous product. Repeated fractional crystallisation, however, from large volumes of acetic anhydride eventually yielded a substance (5.6 grams), which gave crystals with nitrobenzene, and by now employing the latter solvent a product, melting at 329–330°, was eventually isolated. An acetyl determination gave the following result:

Found:  $C_{14}H_6O_{10} = 57.70$ .

$C_{14}O_{10}(C_2H_3O)_6$  requires  $C_{14}H_6O_{10} = 57.00$  per cent.

Evidently, therefore, this compound consisted of a slightly impure acetylcaeruleoellagic acid, and it was subsequently observed that the complete purification of the colouring matter prepared by this arsenic method can only with certainty be effected by means of the benzoyl derivative. For this purpose the partly purified acetylcaeruleoellagic acid is hydrolysed, and the free colouring matter benzoylated according to the method given above. To the hot semi-solid product a trace of alcohol is added, the crystals collected while the mixture is hot, washed with a concentrated solution of benzoic anhydride in alcohol, and finally with alcohol. By a second treatment in a similar manner, pure benzoylcaeruleoellagic acid



(Found,  $C=70.05$ ;  $H=3.26$ ), melting at about  $340^{\circ}$ , could be isolated.

A benzoyl determination gave  $C_{14}H_6O_{10}=35.53$  per cent., and analyses of the free colouring matter (Found,  $C=50.40$ ;  $H=1.98$ ) and of its acetyl derivative (Found,  $C=53.08$ ;  $H=3.24$ ) showed that there could be no doubt that caeruleoellagic acid is produced when flavellagic acid dissolved in sulphuric acid is oxidised with arsenic acid.

Experiments with the object of improving this process were carried out with disappointing results. Thus it was observed that by employing at  $130^{\circ}$  larger amounts of arsenic acid the yield of the crude substance was further decreased, although it contained a somewhat larger percentage of caeruleoellagic acid, and again an excess of arsenic acid at  $120^{\circ}$  for a shorter period gave very little caeruleoellagic acid, but, on the other hand, in this case the oxidation was of a less destructive character.

The mother liquors obtained during the isolation of acetyl-caeruleoellagic acid contained a considerable quantity of acetyl-flavellagic acid, the presence of which was indicated by an acetyl determination (Found,  $C_{14}H_6O_9=60.22$  per cent.), and by the fact that with boiling concentrated potassium hydroxide solution it gave hexahydroxydiphenylmethylid, the acetyl derivative of which melted at  $230-233^{\circ}$ .

Ellagic acid behaves similarly to flavellagic acid when its solution in sulphuric acid is treated with arsenic acid at  $130^{\circ}$ . An insoluble arsenic derivative at first separates, a brisk effervescence ensues, and a rich brown liquid is ultimately produced. The crude product of the reaction, which is soluble in dilute alkali with a pure blue colour, is best purified by the fractional crystallisation of the acetyl derivative, and subsequently of the benzoyl compound. An acetyl determination of the former gave  $C_{14}H_6O_{10}=57.23$  per cent., whereas the figures obtained by the analysis of the benzoyl compound were  $C=70.26$ ;  $H=3.39$  per cent.

If a trace of arsenic acid is added to caeruleoellagic acid dissolved in warm sulphuric acid a yellow, curdy precipitate is produced, and this on further heating disappears, with the formation of a deep blue solution. Flavellagic acid behaves similarly, giving a bluish-violet liquid, whereas in the case of ellagic acid the precipitate at first produced merely dissolves with an orange-yellow coloration. When distilled with zinc dust, caeruleoellagic acid yielded a small quantity of oily matter, which on keeping partly solidified. This, after crystallisation from alcohol, formed leaflets having a faint pink coloration, which melted at  $111-113^{\circ}$ , and evidently consisted of fluorene.

To a boiling mixture of 25 c.c. of water, 25 grams of potassium hydroxide, and 50 c.c. of alcohol, 5 grams of caeruleoellagic acid were added, and the digestion continued until the upper alcoholic layer had distilled off. The product diluted with water was at once poured into acid, the deep brown liquid allowed to remain overnight, and filtered from a small deposit of caeruleoellagic acid which had then separated. The clear liquid was repeatedly extracted with ethyl acetate, the extracts evaporated, and the greyish-white residue crystallised two or three times from water. This compound can also be obtained when aqueous potassium hydroxide is alone employed, but the reaction proceeds better in the presence of alcohol, for air-oxidation is thus almost entirely avoided:

Found: C=51.24; H=3.67.

$C_{12}H_{10}O_8$  requires C=51.06; H=3.54 per cent.

It consists of an almost colourless, crystalline powder, soluble in dilute potassium hydroxide solution with a reddish-violet coloration, which becomes brown on exposure to the air. With ferric chloride it gives a deep brown colour, and with lead acetate solution a nearly colourless precipitate, which quickly develops a bluish-black tint. Nitric acid gives a deep yellow coloration.

The acetyl derivative is prepared by a short digestion of the substance with boiling acetic anhydride containing a trace of pyridine. Addition of alcohol caused the deposition at first of a viscous precipitate; this was removed, and the clear liquid allowed to remain overnight. The crystals which had then separated were purified by recrystallisation from a mixture of alcohol and acetic acid:

Found: C=54.28, 54.31; H=4.60, 4.47.

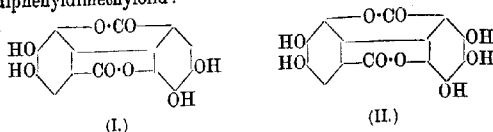
$C_{12}H_8O_8(C_2H_5O)_8$  requires C=54.27; H=4.20 per cent.

It forms colourless needles, melting at 177–178°, and when hydrolysed with a little boiling dilute sulphuric acid deposits the phenol in prismatic needles.

There can be little doubt that this compound,  $C_{12}H_{10}O_8$ , is in reality an *octahydroxydiphenyl*, and in its general properties it indeed somewhat closely resembles the so-called  $\beta$ - and  $\gamma$ -hexahydroxydiphenyls obtained from ellagic acid by Barth and Goldschmidt (*Ber.*, 1879, 12, 1244). Although not itself a dyestuff, with iron and aluminium mordanted calico it gives respectively bluish-black and reddish-brown shades, but these colours are evidently due to an oxidation product of the parent substance.

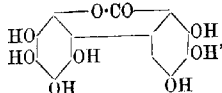
It has been shown by Perkin and Nierenstein (*Trans.*, 1905, 87, 412) and Perkin (*ibid.*, 1906, 89, 251) that ellagic acid (I) is the

tetrahydroxy- and flavellagic acid (II) the pentahydroxy-derivative of diphenyldimethylid:

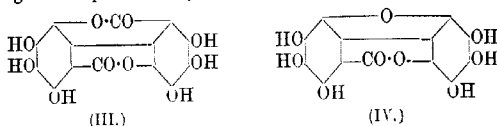


and that by means of boiling concentrated potassium hydroxide solution these colouring matters respectively yield pentahydroxy- and hexahydroxy-diphenylmethylid, although the reaction in the second case proceeds more readily.

Numerous experiments under varied conditions have failed to produce from caeruleoellagic acid the anticipated heptahydroxy-diphenylmethylid:



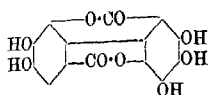
and on this account a doubt at first existed as to whether it in reality possessed the constitution of a dihydroxyellagic acid (III), or might be represented by the formula (IV):



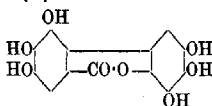
Thus the analytical figures required for both these formulæ and for the corresponding acetyl and benzoyl derivatives show a fairly close agreement, and both compounds constituted in this manner should yield fluorene when distilled with zinc dust. The possibility that caeruleoellagic acid, however, possessed the second of these constitutions was eventually negated by the production from it of octahydroxydiphenyl.

The ready decomposition of caeruleoellagic acid with alkali in the manner above described is not so difficult to understand when the constitution which has been assigned to it (dihydroxyellagic acid) is considered. The first product of the reaction will consist of octahydroxydiphenyldicarboxylic acid, and it is to be anticipated that this compound, containing as it does both the carboxyl groups in the ortho-position with respect to hydroxyl groups, would in these circumstances readily lose two molecules of carbon dioxide, without the intermediate formation of the monocarboxylic acid corresponding with heptahydroxydiphenylmethylid. In the case

of flavellagic acid (I) the ease with which this suffers conversion into hexahydroxydiphenylmethyloid (II) is, on the other hand,



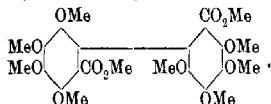
(I.)



(II.)

evident, because the heptahydroxydiphenyldicarboxylic acid produced by means of the alkali contains one of the carboxyl groups in the more stable meta-position.

A further proof of the constitution of caeruleoellagic acid could no doubt be obtained by an investigation of its behaviour when methylated according to the method applied by Herzig and Polak (*Monatsh.*, 1908, **29**, 263) and Herzig and Bronneck (*ibid.*, 1908, **29**, 281) to ellagic and flavellagic acids. In this manner caeruleoellagic acid should yield the compound:



but with the desire of not trespassing on the domain of these authors a study of this reaction was not attempted.

Whereas ellagic and flavellagic acid are obtained when gallic acid is oxidised by means of potassium persulphate and sulphuric acid (*loc. cit.*), it suggested itself that by working at a higher temperature and employing an excess of the reagent, caeruleoellagic acid might be prepared by this method. An experiment indicated that such is probably the case, for the crude product of the reaction dissolved in dilute alkaline solutions with a somewhat bluer tint than that given in these circumstances by flavellagic acid itself. The main bulk of the substance was, however, flavellagic acid, and it was not found possible by a use of the methods described above to isolate the very small quantity of caeruleoellagic acid which appears to be present in the mixture.\*

Caeruleoellagic acid possesses well-marked dyeing properties of a similar character, although more strongly developed than those of ellagic and flavellagic acids, and may have practical utility. Owing to its sparing solubility, it gives the best results in the paste form, for which purpose it is preferably dissolved in hot sulphuric acid,

\* Experiments with the object of introducing further hydroxyl groups into caestellagic acid, the dihydroxydiphenyldimethyloid derived from protocatechuic acid by means of arsenic and sulphuric acids, or by the action of sulphuric acid at high temperatures, have given negative results.

precipitated by water, and thoroughly washed. The following results were obtained by employing mordanted woollen cloth.

Chromium.	Aluminium.	Tin.	Iron.
Deep olive-yellow.	Greenish-yellow.	Dull yellow.	Greenish-black.

In the case of the aluminium mordant the employment of chalk in the dye-bath exerts a detrimental effect.

By the inclusion of Herzig and Tscherne's resoflavin (*Annalen*, 1907, **351**, 24), prepared by the oxidation of 3:5-dihydroxybenzoic acid, a series of hydroxydiphenyldimethylolid derivatives is now known to exist:

Metellagic acid, $C_{14}H_5O_4(OH)$ .	Ellagic acid, $C_{14}H_2O_4(OH)_4$ .
Catellagic acid, $C_{14}H_4O_4(OH)_2$ .	Flavellagic acid, $C_{14}HO_4(OH)_5$ .
Resoflavin, $C_{14}H_3O_4(OH)_3$ .	Caeruleocellagic acid, $C_{14}O_4(OH)_6$ .

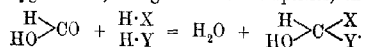
CLOTHWORKERS RESEARCH LABORATORY,  
THE UNIVERSITY, LEEDS.

#### CLXIV.—*The Interaction of Formic Acid and Cellulose.*

By CHARLES FREDERICK CROSS and EDWARD JOHN BEVAN.

PRODUCTS of interaction of cellulose and formic acid have been described in various communications (Berl and Smith, *Ber.*, 1907, **40**, 906; R. C. Woodbridge, *J. Amer. Chem. Soc.*, 1909, **31**, 1067) and patent specifications, and it is generally assumed that such products are formed by a process of simple esterification. The probability of formic acid reacting in more than one way should, however, be taken into account, and also, as a factor in the reaction, the labile equilibrium of the cellulose complex and its tendency to change its configuration under the action of reagents (*Trans.*, 1904, **85**, 691).

The possible modes of action of formic acid are in addition to the normal replacement of alcoholic hydroxyl groups by the O·COH residue: (1) As a consequence of the avidity of the acid, an attack on the cellulose complex by hydrolysis or condensation, or by both processes concurrently. (2) The acid may react through its carbonyl oxygen atom, and give rise to complexes, thus:



As regards the cellulose we cannot pretend to predict the course of change or the final equilibrium under (1); and under (2), if reaction takes place, it suggests the existence in cellulose of pre-formation according to (1) of  $\text{CH}_2\text{CO}$  groupings. This is an

ypothesis justified by well known transformations of the carbohydrates (as in the production of levulic acid from the hexoses), and more particularly of cellulose under the action of acids.

These considerations have been formulated as the result of an investigation of typical derivatives of this group manufactured by processes already worked on the industrial scale. These compounds are found to be divergent in properties and general characteristics from what might be accepted as the normal, defined from analogy of the better known esters, and especially the acetates.

#### EXPERIMENTAL.

The products which we have more particularly studied were prepared and supplied to us by Professor Dr. E. Bronnert (Mulhouse), and were (a) a voluminous, white solid, and (b) a transparent film, (a) being the direct product of interaction of formic acid and cellulose (without catalyst), and (b) being obtained by spreading a solution of (a) on a glass surface, and evaporating the solvent acid.

*Examination of (a):*—The product was soluble in pyridine and nitrobenzene; a characteristic solvent was found in the alkali thiocyanates (for example, of potassium and ammonium); a 20 per cent. solution of these salts dissolved the compound freely.

When dried in the air the substance contained 8–9 per cent. of water.

After swelling with pyridine, the action of  $N/2$ -aqueous-alcoholic sodium hydroxide was rapid:

Found: Acid (as  $\text{CH}_2\text{O}_2$ ) = 44.0. Residue (cellulose) = 76.6.

Cellulose diformate requires Acid (as  $\text{CH}_2\text{O}_2$ ) = 43.2;

Residue (cellulose) = 74.3 per cent.

Under the direct action of the  $N/2$ -alkali, the saponification is less rapid, and higher acid numbers are obtained ( $\text{CH}_2\text{O}_2$  = 46 per cent.) as a result of long-continued action.

On analysis of the anhydrous compound the following numbers were obtained:

0.1498 gave 0.2425  $\text{CO}_2$  and 0.0712  $\text{H}_2\text{O}$ . C = 44.15; H = 5.38.

$\text{C}_7\text{H}_{10}\text{O}_6$  (monoformate) requires C = 44.2; H = 5.26 per cent.

These numbers do not correspond with the composition represented by the results of saponification. In other elementary analyses there was a still closer approximation to the numbers for cellulose, and therefore further divergence from the theoretical numbers for a diformate, which requires C = 44.0; H = 4.58 per cent. These variations were probably due to the fact that the compound proved to be unstable.

After being kept for four months (in a closed bottle) it was no

longer soluble in pyridine, and was found to have developed acidity; it contained free acid (calculated as  $\text{CH}_2\text{O}_2$ ) equal to 10·9 per cent. of its weight. After removing this free acid, the compound was boiled with water. Further volatile acid distilled over, which amounted to 10·8 per cent., a total of 20·8; the loss of formic acid (1 mol.) from a diformate should be 21·1 per cent. As an explanation of these results we may assume that the original compound is a monoformate, but of a modified cellulose complex, the second molecule of formic acid, obtained on saponification, being a product of decomposition of this complex, and this is confirmed by the following experiments.

*Acetylation*.—The compound was mixed with 10 parts of acetic anhydride at  $50^\circ$ , and a 15 per cent. solution of zinc chloride in glacial acetic acid was added; the substance dissolved completely. The solution was boiled in one experiment for one hour, and in a second for five minutes, and the new ester precipitated by pouring into water.

The yield in both cases was the same, namely, 120 per cent., and corresponds with the subjoined numbers defining the composition of the product. On analysis:

0·1725 gave 0·3301  $\text{CO}_2$  and 0·0769  $\text{H}_2\text{O}$ .  $\text{C}=47·48$ ;  $\text{H}=4·96$ .

$\text{C}_{11}\text{H}_{14}\text{O}_8$  (a diaceto-monoformate) requires  $\text{C}=48·18$ ;

$\text{H}=4·75$  per cent.

This diaceto-monoformate neutralised 46 per cent. of its weight of sodium hydroxide, and gave an insoluble residue (cellulose)=54·5. ( $\text{C}_{11}\text{H}_{14}\text{O}_8$  requires  $\text{NaOH}=46$ ; cellulose=59·1 per cent.) The amount of cellulose found was as usual low, owing to unavoidable further hydrolysis. When dried in the air the compound retained 1·5 to 2·0 per cent. of moisture, which is within the normal low limits characteristic of the true esters.

The instability of the original ester is thus also shown on acetylation, as one formyl group is displaced when two acetyl groups enter the molecule.

There is, however, further evidence as to the constitution of the original ester, confirming the view that in the reaction by which it is produced the cellulose complex undergoes constitutional modification.

(1) A careful examination of the acid products of saponification, using aqueous sodium hydroxide only, showed that acetic acid is produced. The acid was separated by fully oxidising with permanganate the volatile acids first obtained, redistilling, and finally crystallising the silver salt. (Found:  $\text{Ag}=64·85$ . Calc.,  $\text{Ag}=64·65$  per cent.)

The acetic acid thus formed must be a product of resolution of the new cellulose complex.

(2) The cellulose residue showed divergencies from the normal; thus, on analysis:

0.1300 gave 0.2133  $\text{CO}_2$  and 0.0810  $\text{H}_2\text{O}$ .  $\text{C}=44.60$ ;  $\text{H}=6.93$ .

The value for hydrogen is an indication of the production of methyl groups, involving, therefore, the migration of hydroxyl groups within the cellulose complex.

This "cellulose" was acetylated, and gave a high yield (185 per cent.) with an exceptionally high acid number on saponification acid (as  $\text{C}_2\text{H}_4\text{O}_2$ ) = 81.1] and correspondingly low cellulose residue (27.3). These numbers and relations are sufficient to indicate the more complex nature of the interaction of cellulose and formic acid (*supra*). Further investigation is required for the full elucidation of the constitutional modification which cellulose appears to undergo.

*Examination of (b)*:—This was a transparent uniform film of 0.085 mm. thickness. From the dimensions we were able to estimate closely the volume of a given weight, the specific gravity being found to be 1.520; that is, in the normal air-dry state. The moisture retained in this condition was 13.0–16.0 per cent. Both figures are widely divergent from those generally characteristic of the cellulose esters. The film was found to resist the general solvents of these esters, as well as the special solvents noted for the product (a). Analysis gave:

Anhydrous substance:

0.1281 gave 0.2052  $\text{CO}_2$  and 0.0744  $\text{H}_2\text{O}$ .  $\text{C}=43.7$ ;  $\text{H}=6.4$ .

0.1454 " 0.2355  $\text{CO}_2$  " 0.0812  $\text{H}_2\text{O}$ .  $\text{C}=44.1$ ;  $\text{H}=6.2$ .

$\text{C}_6\text{H}_{10}\text{O}_5$  requires  $\text{C}=44.4$ ;  $\text{H}=6.1$  per cent.

Air-dried substance:

0.1579 gave 0.2224  $\text{CO}_2$  and 0.0988  $\text{H}_2\text{O}$ .  $\text{C}=38.4$ ;  $\text{H}=6.8$ .

$\text{C}_6\text{H}_{10}\text{O}_5 + \text{H}_2\text{O}$  (15.8 per cent.) requires  $\text{C}=38.39$ ;

$\text{H}=6.85$  per cent.

So far, therefore, there is nothing to identify this product as an ester; it has the composition and properties of a cellulose.

Saponification of the substance with  $N/2$ -aqueous-alcoholic sodium hydroxide proceeded with some difficulty. The following results were obtained:

Duration of boiling.	Acid formed, calc. as $\text{CH}_2\text{O}_2$ .
9 hours	25.0
Further 6 "	12.1
" 4 "	4.4
	<hr/> 41.5

These results indicate a course of action different from the saponification of an ester: rather a progressive decomposition of a cellulose complex with production of acid groups.

With the view of elucidating this point, we carried out some experiments on the interaction of formic acid and typical celluloses.



(a) Cotton, wood, and esparto celluloscs were taken as types of the generally accepted classification. The action in these cases is slow, and accompanied by considerable discoloration (brown). Products of condensation are formed. The fibres gelatinise, showing progressive hydration, and the action differs markedly from that of other acids comparable in general functions with formic acid.

On treating with water and washing, we obtained:

Percentage of original.	Cotton.	Wood cellulose.	Esparto.
Insoluble product .....	99.0	91.0	82.5
In solution .....	5.7	11.4	—
Total .....	104.7	102.4	—
Saponification of insoluble product:			
yield of acid as $\text{CH}_2\text{O}_2$ .....	13.11	22.45	26.2

It is to be noticed that with a small gain of weight due to the fixation of the formyl residue, there is a relatively large production of acid on saponification. In other words, the celluloses are constitutionally modified, and, as a result, are decomposed by alkalis with the formation of acid products.

(b) Cellulose (hydrate) regenerated from solution as xanthate (viscose).

On digestion at  $60^\circ$  there is a very gradual attack, the cellulose passing into a viscous solution. On dilution, the product is precipitated. The following determinations were made:

(1) Twelve hours' digestion—incomplete solution.

(2) Twenty-four hours' digestion—nearly complete solution.

	(1.)	(2.)
Reprecipitated .....	89.4	85.42
Products in solution:		
(Residue on evaporation) .....	20.4	35.80
	109.8	121.22

The insoluble product from (2) on saponification showed acidity equal to 44.00 (calc. as  $\text{CH}_2\text{O}_2$ ). These numbers and incidental observations lead to the conclusion that this form of cellulose (hydrate) is attacked without formation of condensed coloured products. There is no discoloration, even on raising the temperatures to  $100^\circ$ , and the viscosity persists when the heating is long continued; at the same time a portion of the cellulose is degraded to soluble products of low molecular weight. These products were acid in higher proportion. We have also made a comparative study of the interaction of formic acid (99 per cent.) and the hydrated celluloses obtained from solutions in cuprammonium, and as xanthic ester (viscose). These show similar behaviour. With the acid alone, prolonged digestion at temperatures up to  $45^\circ$  failed to effect more than partial solution (30 per cent.). The presence of catalysts effects a marked change. With 20 parts

of the acid containing 2 per cent. of zinc chloride in solution, a homogeneous product was obtained in twenty hours' digestion at 50°. The purified product was analysed:

0.1713 gave 0.2758 CO<sub>2</sub> and 0.0716 H<sub>2</sub>O. C=43.91; H=4.65.

A diformate requires C=44.0; H=4.58 per cent.

With phosphoric acid the action is especially rapid. In a typical case, we obtained a yield of 116 per cent. of the insoluble product, which on saponification gave, acid (as CH<sub>2</sub>O<sub>2</sub>)=49.5 and residue (cellulose)=56.4 per cent.

Owing to the difficulties inherent in investigations of cellulose products it will be necessary to extend these observations to other polyhydroxy-compounds of which the products of possible decomposition are better known, or which, from simplicity of molecular structure, can be studied in relation to synthetic reaction with greater precision of data.

In one direction we have examined starch, which shows many analogies to cellulose in its reaction with formic acid; products insoluble in water are obtained, and these also, on saponification, show acidity in excess of the molecular proportions of acid actually combining. We have also studied certain aromatic compounds under similar conditions of interaction, and although there is no direct relationship of these to cellulose, it is well known that, through the lignocelluloses, there are many suggestions of a cyclic constitution of cellulose.

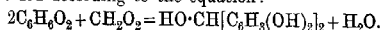
The following is a brief account of the results obtained with typical aromatic hydroxy-compounds.

*Resorcinol* reacts with formic acid, and in the presence of hydrochloric acid the change is rapid, a substance being formed with considerable development of colour (crimson). The main product is easily isolated by crystallisation from water:

0.1482 gave 0.3397 CO<sub>2</sub> and 0.0714 H<sub>2</sub>O. C=62.5; H=5.3.

C<sub>12</sub>H<sub>10</sub>O<sub>6</sub> requires C=62.9; H=4.8 per cent.

The formula suggests that the compound is a *dihydroxybenzhydrol*, formed according to the equation:



The alkaline solutions of this substance are very strongly coloured (crimson). The *penta-acetyl* derivative was recrystallised from alcohol:

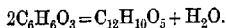
0.250 gave C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>=67.2.

C<sub>25</sub>H<sub>22</sub>O<sub>10</sub> requires C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>=65.5 per cent.

*Quinol* gives no reaction under similar conditions, and it appears, therefore, that condensation takes place in the para-position with respect to a hydroxyl group. This is confirmed by experiments on α- and β-naphthol. The latter does not react with formic acid, whilst the former gives a small amount of a condensation product,

which is insoluble in water, but reacts with alkalis, giving grass-green solutions. The reaction of the naphthols with acetaldehyde are analogously divergent (Claisen, *Ber.*, 1886, **19**, 3316).

*Phloroglucinol* reacts rapidly, but the first product appears to be phloroglucide (Found, C=61.3; H=4.0. Calc., C=61.4; H=4.2 per cent.), which would be formed according to the equation:

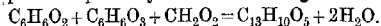


With resorcinol and phloroglucinol in molecular proportions, we obtained intermediate results; the main product after crystallisation was analysed:

0.1360 gave 0.3229 CO<sub>2</sub> and 0.0468 H<sub>2</sub>O. C=64.7; H=3.8.

C<sub>13</sub>H<sub>10</sub>O<sub>5</sub> requires C=63.4; H=4.0 per cent.

This compound is probably formed according to the equation:



To connect these observations with cellulose it is only necessary to remember that the CH . . . OH(1:4) grouping of a phenol alternates with, and, in fact, reacts as, the grouping CH<sub>2</sub> . . . CO, and a keten grouping has been shown by ourselves to be definitely characteristic of the lignocelluloses and inferentially of the celluloses ("Cellulose," 1895, and "Researches on Cellulose," I. and II., 1900-1905). Collie has developed the potentialities of the keten and multiple keten group from a broader point of view, and applies his conclusion to the carbohydrates, including cellulose (*Trans.*, 1907, **91**, 1806).

From the results so far obtained we may conclude that the formyl derivatives of cellulose are not the analogues of the acetates, the reactions of formation certainly introducing other factors which we have indicated, and our further investigations will have reference to the influence of these, as a working hypothesis.

Incidentally, these results suggest a clue to anomalies, and the apparently contradictory results of investigators in regard to the acetates of cellulose (Berl and Smith, *loc. cit.*; Ost, *Zeitsch. angew. Chem.*, 1906, **19**, 993; J. Gutsche, *Diss.*, Göttingen, 1910), which we shall discuss in a subsequent communication.

We are indebted to Professor Bronnert for the supply of products as stated, and we have pleasure in acknowledging experimental results included in this paper from Mr. S. S. Napper, and our indebtedness to Messrs. S. Courtauld and Co. for their valuable collaboration. We wish also to mention the efficient services of our assistant, Mr. D. R. Davey, throughout these investigations.

4, NEW COURT,  
LONDON, W.C.

## OBITUARY NOTICE.

## JAMES CAMPBELL BROWN.

BORN JANUARY 31ST, 1843; DIED MARCH 14TH, 1910.

JAMES CAMPBELL BROWN was born at Aberdeen on the 31st of January, 1843. His father was Mr. George Brown, of Messrs. G. Brown and Co., Alum Works, Bow Common, London. He came of an old Scottish family, connected by marriage with the Grahams, Dukes of Montrose and the Earls of Strathmore. As a boy he attended the Gymnasium in Old Aberdeen, a famous school in its day, by reason of the character and attainments of its head, Dr. Alexander Anderson. In 1857 he entered Marischal College in Aberdeen, and attended the classes there in Latin and Greek; subsequently he passed through the classes of the first two years of the medical curriculum, specially distinguishing himself in botany and chemistry. Originally he had intended to take up medicine as a profession, but his interest in science had been aroused, and in 1863 he proceeded to London to study under Tyndall and Hofmann at the Royal College of Chemistry, and also at the School of Mines. He matriculated in 1862 at the London University, obtained the degree of Bachelor of Science in 1867, with first class honours in chemistry, and the degree of Doctor of Science in 1870. In 1907 the University of Aberdeen conferred on him an honorary degree of LL.D. His career as a teacher began in 1864, when he was appointed assistant to the Professor of Chemistry at Aberdeen University. In 1867 he was appointed lecturer in Experimental Science and Toxicology at the Liverpool Royal Infirmary School of Medicine. Henceforward to the end of his life he was associated with Liverpool. In 1872 he married Ellen Fullerton (daughter of John Henderson, of Quarry Lodge, Aberdeenshire), who survives him.

During the whole forty-three years he was connected with Liverpool he was keenly interested in education; and the present generation of teachers in the North are perhaps not fully aware how much they owe to Professor Campbell Brown. In 1877, ten years after he came to Liverpool, he had become Chairman of the Royal Infirmary School of Medicine. It was at this period that he and the late Mr. W. J. Stewart, stipendiary magistrate of Liverpool, were elected joint-secretaries of the committee for organising a University College in Liverpool; the amount of work done in con-

nexion with this committee must have been very great, and as an organiser Dr. Campbell Brown came prominently to the fore.

When the School of Medicine was merged in the newly-formed College, two Chairs were founded to take the place of the lectureship in Experimental Science. The Chair of Physics was occupied by Professor Lodge (now Sir Oliver Lodge), and the Grant Chair of Chemistry by Professor Campbell Brown. Henceforward, he never spared himself in efforts that might benefit the development of his department or the training of students. His heart was bound up in the success of the chemical school, and to the time of his death improvements and additions were being made in the laboratories.

There are many men who are proud to have studied under him, and there are many more who owe to him their first start in life, for he took immense trouble in finding suitable posts for his students when they had to leave the College. He was in intimate touch with the chemical manufacturers of Lancashire and Cheshire, and was able to supply them with well-trained men.

In 1884 the chemical laboratories at University College, Liverpool, were built, and further extensions were made by 1886. In the session 1896-7 the William Gossage Laboratory was opened, and rooms were added for metallurgy, electro-chemistry, and gas analysis. Recognising that electro-chemistry was a subject of great importance in University training, Professor Campbell Brown obtained the help necessary for the founding of a lectureship in that subject, and soon afterwards, by the help of Mr. Muspratt and Sir J. Brunner, the Muspratt laboratories were built.

Besides being connected with the University College of Liverpool, Professor Campbell Brown was a public analyst as well, and his services to the community in suppressing the adulteration of food were of the greatest value. In 1872 he was appointed public analyst to the city of Liverpool, in 1873 he was also appointed to the same post for Cheshire and the Isle of Man, and in 1875 for Lancashire. The latter position he retained till his death. He was an original member of the Society of Chemical Industry, and also of the Society of Public Analysts. He was elected a Fellow of this Society in 1867, and was one of our Vice-Presidents when he died on March 14, 1910.

Professor Campbell Brown was always an enthusiastic advocate for investigation and research, and there were very few years during the period 1870-1910 in which he published nothing. His earliest paper in 1870 was on "The artificial formation of organic compounds," and his last was published after his death in the *Transactions of the Chemical Society*, the title being: "An apparatus for the study of the reaction between organic compounds and inorganic compounds."

his for the distillation of fats and fatty acids in the vacuum of the cathode light."

The ground covered in his original communications was very wide; pure and applied chemistry, analytical, toxicological, and botanical subjects are all represented. Perhaps his principal contribution to applied chemistry, at least the one that was of immediate and great practical value, was a report published in 1874 on the agricultural chemistry of the plantations of India. This was the outcome of a long series of analyses of healthy and unhealthy tea plants, and of the soils in which the tea plant was growing. The result of this work was the devising of a fertiliser for use in the plantations, which proved remarkably successful, but he never took any steps to secure for himself a pecuniary interest in the extensive use to which this fertiliser was put.

The bulk of his earlier publications were on analytical subjects; analysis of butter, pepper, and other substances; and his experience in this branch of chemistry was very large indeed. He was always trying in every way to suppress the adulteration of food. In the early days, when he was appointed public analyst for Liverpool under the Adulteration of Foods Act, this was no easy task. It was he who had to plan and superintend the building of the chemical laboratories, and organise routine methods for the analysis of foods and drugs on the large scale.

He was always ready to do all in his power for the purpose of raising the profession of the public analyst, and he recognised that the most important factor in an analyst's work was accuracy. In his own analytical laboratories his method was always to have every analysis repeated in its essential portion by a second operator, and, when possible, by a different method, thus as far as possible avoiding error. His zeal for "precise" methods and his dissatisfaction with all others was one of his most characteristic points.

He was also appointed analyst to the Water Committee of the City of Liverpool, and to all the local authorities in the administrative county of Lancaster. He was frequently consulted in reference to large schemes of public water supply, such as Hawes Water, the Vyrnwy watershed, the Liverpool supply, the new Birmingham supply, the Birkenhead supply, and others. His experience in this subject is, in part, embodied in various papers, for one of which, "Deposits in pipes and other channels carrying potable waters," he was awarded, in 1904, the "Manby Premium" by the Council of the Institute of Civil Engineers. As a toxicologist, he had a large experience, especially in cases connected with arsenic poisoning.

Apart from chemistry, Professor Campbell Brown was a many-

sided man, a distinguished botanist, a lover of music and literature, and a great lover of nature.

At his property at Wedderhill, near to Stonehaven, he made a wonderful Alpine garden, full of every kind of Alpine plant, which was an endless source of enjoyment to him in after years. To those who knew him well, Professor Campbell Brown was a man of whom it is particularly hard to have to say "We shall see him no more." Honest, sturdy, straightforward, kindly, and with a keen sense of humour, he went through life doing good to everyone.

As a teacher and organiser, the University of Liverpool owes him a deep debt of gratitude. The chemical world has lost a member who, in all his scientific work, always set before himself the ideal that if a thing was worth while doing, it was worth while doing well.

At the close of a long life, to his honour be it said, he was still engaged in research, in most important public duties, and in ensuring that his students began their lives as well-trained and competent chemists.

H. B. D. and J. N. C.

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## ERRATA.

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## PART I.

Page	Line	
1068	1*	for " $\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{C}\begin{smallmatrix} \text{NH}\cdot\text{CH} \\ \text{CH:N} \end{smallmatrix}$ " read $\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{C}\begin{smallmatrix} \text{NH}\cdot\text{CH} \\ \text{CH:N} \end{smallmatrix}$

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## PART I.

547	14	} for " <i>Chlorohistidinecarboxylic</i> " read " <i>Chlorohistinecarboxylic</i> ."
547	18	
547	22*	
880	6*	
Part II.		
1146	11*	} for " <i>histidinecarboxylic</i> " read " <i>histinecarboxylic</i> ."
col. ii.		

VOL. XCIV (ABSTR., 1908).

## PART I.

694	8	} for " <i>chlorohistidinecarboxylic</i> " read " <i>chlorohistinecarboxylic</i> ."
	12	
	14	
	19	
	22	
694	13	for " <i>nitrate</i> " read " <i>nitrite</i> ."

VOL. C (ABSTR., 1911).

i, 157	23	for " <i>1-phenylquinoline</i> " read " <i>2-phenylquinoline</i> ."
i, 181	20*	" <i>REYNAUD</i> " read " <i>RAYNAUD</i> ."
i, 211	9*	" <i>GIUSEPPE</i> " read " <i>GUIDO</i> ."
i, 405	9	" <i>4-m-Xyleneazo-5-hydroxy-4-methylpyrazole</i> " read <i>"4-m-Xyleneazo-5-hydroxy-3-methylpyrazole."</i>
i, 457	18	" <i>furfuran-2-carboxylate</i> " read " <i>furan-2-carboxylate</i> ."
ii, 48	2*	" <i>TAKAHASTU</i> " read " <i>TAKAHASHI</i> ."
ii, 186	27	" <i>Ion</i> " read " <i>Iron</i> ."
ii, 200	3*	" <i>Nitrosulphonic</i> " read " <i>Nitrososulphonic</i> ."
ii, 312	9	" <i>BROWING</i> " read " <i>BROWNING</i> ."
ii, 537	5*	" <i>HEIDUSCKA</i> " read " <i>HEIDUSCHKA</i> ."
ii, 551	2*	" <i>JAVILIER</i> " read " <i>JAVILLIER</i> ."

\* From bottom.





tus for the distillation of fats and fatty acids in the vacuum of the cathode light."

The ground covered in his original communications was very wide; pure and applied chemistry, analytical, toxicological, and botanical subjects are all represented. Perhaps his principal contribution to applied chemistry, at least the one that was of immediate and great practical value, was a report published in 1874 on the agricultural chemistry of the plantations of India. This was the outcome of a long series of analyses of healthy and unhealthy tea plants, and of the soils in which the tea plant was growing. The result of this work was the devising of a fertiliser for use in the plantations, which proved remarkably successful, but he never took any steps to secure for himself a pecuniary interest in the extensive use to which this fertiliser was put.

The bulk of his earlier publications were on analytical subjects; analysis of butter, pepper, and other substances; and his experience in this branch of chemistry was very large indeed. He was always trying in every way to suppress the adulteration of food. In the early days, when he was appointed public analyst for Liverpool under the Adulteration of Foods Act, this was no easy task. It was he who had to plan and superintend the building of the chemical laboratories, and organise routine methods for the analysis of foods and drugs on the large scale.

He was always ready to do all in his power for the purpose of raising the profession of the public analyst, and he recognised that the most important factor in an analyst's work was accuracy. In his own analytical laboratories his method was always to have every analysis repeated in its essential portion by a second operator, and, when possible, by a different method, thus as far as possible avoiding error. His zeal for "precise" methods and his dissatisfaction with all others was one of his most characteristic points.

He was also appointed analyst to the Water Committee of the City of Liverpool, and to all the local authorities in the administrative county of Lancaster. He was frequently consulted in reference to large schemes of public water supply, such as Hawes Water, the Vyrnwy watershed, the Liverpool supply, the new Birmingham supply, the Birkenhead supply, and others. His experience in this subject is, in part, embodied in various papers, for one of which, "Deposits in pipes and other channels carrying potable waters," he was awarded, in 1904, the "Manby Premium" by the Council of the Institute of Civil Engineers. As a toxicologist, he had a large experience, especially in cases connected with arsenic poisoning.

Apart from chemistry, Professor Campbell Brown was a many-

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sided man, a distinguished botanist, a lover of music and literature, and a great lover of nature.

At his property at Wedderhill, near to Stonehaven, he made a wonderful Alpine garden, full of every kind of Alpine plant, which was an endless source of enjoyment to him in after years. To those who knew him well, Professor Campbell Brown was a man of whom it is particularly hard to have to say "We shall see him no more." Honest, sturdy, straightforward, kindly, and with a keen sense of humour, he went through life doing good to everyone.

As a teacher and organiser, the University of Liverpool owes him a deep debt of gratitude. The chemical world has lost a member who, in all his scientific work, always set before himself the ideal that if a thing was worth while doing, it was worth while doing well.

At the close of a long life, to his honour be it said, he was still engaged in research, in most important public duties, and in ensuring that his students began their lives as well-trained and competent chemists.

H. B. D. and J. N. C.

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CLXV.—*A Method for the Accurate Volumetric Determination of the Oxygen in Air.*

By HERBERT EDMESTON WATSON (1851 Exhibition Scholar, University College, London).

PROFESSOR P. A. GUYE and the author have recently ascertained that if the atmosphere were calm there would be a considerable reduction in the percentage of oxygen at high altitudes. If the quantity is taken as 21.00 per cent. at the surface, the amount at 1000 m. altitude is only 20.73 per cent. Owing, however, to the presence of winds, it seems very unlikely that there is in reality any detectable difference, unless, as is not impossible, the upper layers of the atmosphere constitute a region of absolute calm.

Sufficient data to throw light on this question are not yet available, and it is with a view to carrying out a large number of analyses of air collected systematically at different altitudes that the apparatus now described has been designed. For this purpose it is necessary to make use of a method which is as accurate as

possible, but at the same time the question of rapidity is also of considerable importance.

In practice, the estimation of the oxygen in air is carried out by removing this element in some suitable way, and determining the amount of residue. Absorption by heated copper, as performed by Dumas and Boussingault (*Ann. Chim. Phys.*, 1841, [iii], 3, 257), involves complicated apparatus, and is slow. The gravimetric method of Leduc (*Compt. rend.*, 1896, 123, 805), in which the oxygen is absorbed by cold phosphorus contained in a closed bulb, is apparently very accurate, but requires twenty-four hours for the absorption to take place, and also involves the weighing of large glass bulbs, an operation which should be avoided if possible.

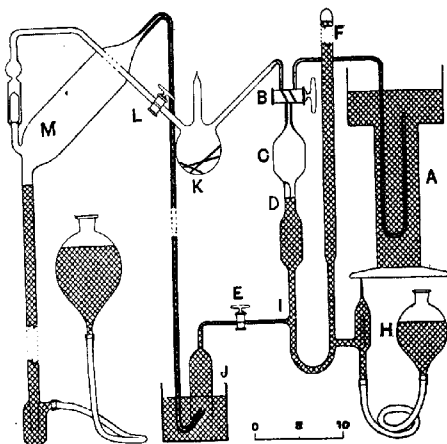
The volumetric method used by Regnault for an exceedingly large number of analyses (*Ann. Chim. Phys.*, 1849, [iii], 26, 329; and 1852, 36, 385) was very simple and rapid, but had several disadvantages. The air was mixed with hydrogen, and exploded, the volume being kept constant, and pressure changes noted. To avoid drying the gas, the measuring tube was always kept moistened with water, thereby probably causing a slight variation in volume. Regnault also applied no compressibility correction, although the error from this cause is very small. In addition, it had been recognised as early as 1836 by De Saussure (*Mem. Soc. de Phys. et d'Hist. Nat. Genève*, 1836, 7, 447) that ammonia was produced by such explosions of hydrogen and air, and to avoid this he devised the elegant, although tedious, method of shaking the air with lead shot and water in a closed bottle, and weighing the amount of water which entered when absorption was complete and the bottle was opened under water.

It is hoped that by means of the present apparatus some of the above-mentioned difficulties may have been eliminated. The general arrangement is shown in the annexed diagram, and it should be noted that special attention is given in the construction to the volumes of the various constituent parts, as this considerably facilitates the subsequent manipulation. Several small details are also important, and will be mentioned as they occur. The construction of the apparatus and the method of using it is best explained by following through the operations carried out in a complete analysis.

The air is introduced into test-tubes with a volume of just over 50 c.c., on the top of which some potassium hydroxide has previously been fused. These are inverted over mercury, and the gas allowed to remain in them at least two hours before analysis in order to remove carbon dioxide and water vapour.

The gas is admitted through the inverted syphon A and the

two-way tap *B* to the burette *C*, but a small quantity of gas must be left behind in the syphon to avoid filling the tube between *B* and *C* with mercury. The height of the mercury is then adjusted by means of the reservoir *H* until it just touches a point *D*, which is set in the middle of a piece of the same tubing as that from which the manometer tube *F* is constructed, both being about 1 cm. in diameter. *F* may be either evacuated, boiled out, and sealed off, or, better, connected to a small pump in which a good vacuum is maintained. The difference of level of the mercury in *F* and at *D* is then read with a cathetometer as well as the meniscus heights in case their difference is sufficient to require the application of a



correction to the pressure. The whole of the burette and the manometer tube is enclosed in a water-jacket (not shown in the diagram) of considerable dimensions, the water being at room temperature. Unless the external temperature is changing very rapidly, it is a matter of no difficulty to maintain the temperature of the water at *C* constant to  $1/50$  of a degree for some time previous to, and during, the measurements.

The bulb *K*, carefully made of thin glass and 60 c.c. in volume, contains about 5 grams of yellow phosphorus. This is introduced before a series of experiments through the tube at the top of the bulb, which is then sealed off, and the bulb evacuated by means of the small Antropoff pump *M* (compare *Chem. Zeit.*, 1910, 34,

979) with a delivery tube not exceeding 0.75 mm. in diameter. After measurement, the air is admitted into *K* (the tap *L* being closed), and the mercury in *C* passed well beyond the tap *B*, which is then turned off. *K* is next heated with a smoky flame for about five minutes, a procedure which appears to absorb the oxygen completely.

After allowing about twenty minutes for the vapours to settle, *B* is opened and *H* lowered until the mercury falls just below the T-join *I*, and half the gas passes back into the burette. *B* is then closed, and the remaining gas pumped into *J*. The volume of *J* being 20 c.c., the gas completely fills it, and no bubbles can stick to the sides. The delivery tube of the pump must, however, always be tapped when all the gas has been pumped off, because a bubble invariably remains on the end unless this is done. The tap *E* is next opened, and the gas from *J* passes into the burette. The total volume of the latter is 60 c.c., so that the pressure inside after the admission of the gas is sufficiently low to cause the mercury to rise in *J* and pass to *I*. The capillary tube between these two points is of 0.5 mm. bore, and very carefully blown on at each end so as to form no hollow in which a bubble of air could catch. It is also necessary to turn the tap right round once or twice to make sure that no bubble remains in the bore. While the mercury is running in from *I*, the reservoir *H* is carefully raised, and it can at once be seen if any air remains at *I*, and, if so, it is quite easy to displace it by again lowering *H*.

The mercury is then again raised to the point *D*, and after a short interval the pressure and temperature are measured, and the gas expelled from the apparatus through *A*.

Allowing fifteen minutes to elapse before taking each pressure reading, twenty minutes for the phosphorus vapours to settle and grow cool, and fifteen minutes for complete evacuation with the pump, the whole analysis may easily be performed in an hour and a-half.

More phosphorus may be introduced from time to time as considered necessary. It is not easy to say for how many analyses a given quantity of phosphorus will suffice, but on one occasion when 2 grams had been used for about ten analyses, it was found that only a small fraction of the whole had been oxidised or converted into the red variety. At intervals the whole bulb *K* may be cut down and cleaned. It should be noticed that the oxides of phosphorus in this bulb form the only drying agent in the apparatus. Since the gas is introduced dry, even this is unnecessary, but it is absolutely essential before starting work for the first time to circulate the dry nitrogen formed in the first combustion through all parts of the apparatus at least three or four times.

The calculation of the results is simple. Since 50 c.c. of air are used for the analysis, it will be seen that after absorption of the oxygen, and when the gas is being again measured, the pressure in the burette is approximately atmospheric, whilst, in addition, the bore of the tap *B* leading to *K* is filled with gas at half this pressure. Any error due to this cause, however, even with a tap of large bore, is automatically eliminated, for it will be observed that this gas remains in the apparatus when the rest is expelled at the end of the experiment. On introducing another sample of air, the volume is measured between the barrel of the tap and the point *D*. The gas remaining in the tap bore from the previous experiment is added to this air when it is admitted to *K*, but an equal volume is again retained in the tap bore at the end of the experiment (assuming, of course, that approximately equal quantities of air are used for each analysis), so that the volume between the barrel of the tap and the point is the true volume of the nitrogen in the added air. It is hardly necessary to add that this tap must be greased as lightly as possible.

Consequently, if  $p$  be the pressure of the air,  $T$  its absolute temperature, and  $p'T'$  the corresponding quantities for the gases remaining after absorption, the percentage of these gases is given by  $100p'T/pT'$ .

It may be remarked that, assuming  $T$  constant, if  $p$  is one atmosphere,  $p'$  is the partial pressure of the residual gases, thereby measuring the proportion in which they occur, or, dealing with volume,  $p'/p$  gives the ratio of the volume of the residual gases measured at their true partial pressure (and corrected to atmospheric pressure, assuming Boyle's law to be true) to the total volume. This is the only rational method of stating results given as percentages, for in any other case, if, for instance, the oxygen and residual gases were both measured separately at atmospheric pressure, the sum of the two separate volumes would not be equal to the volume when mixed. Actually, in these experiments it is better to measure the air under increased pressure and the residues under atmospheric pressure in order to make the barometer readings rather more accurate, but the change in the value of  $p'/p$  when this is done is less than 1 part in 50,000, and consequently negligible.

With regard to the accuracy of the method, in each of the two sets of measurements there are two manometer readings and a temperature determination. The error in each of the former should not exceed  $1/20$  mm., that is to say, 1 part in 15,000, and the temperature should be correct to  $0.02^\circ$ , or 1 part in 15,000. If this be so, the total maximum error in the final result due to these causes is 6 parts in 15,000, although if the apparatus is rigidly

fixed the errors in reading to the fixed point should be less than that given. The chance of this maximum deviation occurring is, moreover, only 1 in 32.

Assuming that a mercury surface can be set to a point with an accuracy of 0.02 mm., the error in volume thus introduced is about 1 in 25,000 for a tube of the size used. It may, however, be necessary to apply a small correction if the height of the meniscus does not remain constant. If the burette is of fairly thick glass, the change of volume with pressure is negligible.

There are two other possible sources of error. First, a bubble of air may adhere to the glass somewhere. If, however, the experiments are carried out as described, this will not be found to occur, and as, moreover, 1 cu. mm. of air can readily be seen, corresponding with  $1/14,000$  of the whole volume, no error should arise from this cause. Secondly, there is the possibility of incomplete absorption by phosphorus. There seems, however, to be every reason to suppose that even if traces of oxygen do remain, the quantities are too small to detect or measure, except by electrical methods. Leduc (*loc. cit.*) could detect no error in his experiments, owing either to insufficient absorption or to the vapour pressure of the phosphorus, and in the present series no variation which could be ascribed to these causes has been observed in the experiments already carried out, although, of course, it is not possible to detect a small constant error.

The following example illustrates the completeness of the absorption, and the safety of circulating the gas through the apparatus. A value of 79.07 was obtained for the percentage of nitrogen on one occasion. The gas was re-measured next morning under quite different temperature conditions, and the figure deduced was 79.09. The gas was then passed into the phosphorus, well heated, pumped off, and again measured, the percentage found being then 79.08.

Below are given some of the preliminary results obtained for various specimens of air. It will be seen that the agreement for different analyses of the same sample is fairly close. With regard to the absolute value, it would seem that the mean percentage of oxygen is slightly higher than that measured by Regnault (*loc. cit.*), that is, 20.952 at Paris, and 20.949 at Geneva, with a maximum value of 21.00, but it should be very close to the figure 21.00 deduced by Leduc for Paris air.



*Results of Some Analyses.*

Source of air.	Percentage of oxygen.		
	20.96	20.93	—
Laboratory, Geneva, 4 p.m., July 11, 1910.....	20.98	20.95	—
" " 5 p.m., " 12, " .....	21.02	21.04	21.02
" " (alt. 800 m.) 10 a.m., May 19.	20.95	20.93	—
Salève (alt. 1800 m.) " " .....	21.02	—	—
Rochers de Naye (alt. 2045 m.) " " .....	21.04	—	—
" " " 5.30 a.m. ....	—	—	—

As already mentioned, the few results obtained are merely preliminary, and it is not intended to discuss their bearing on the composition of the atmosphere in the present paper.

In conclusion, I should like to express my best thanks to Professor P. A. Guye, in whose laboratory this work was carried out, for his help in obtaining some of the samples of air analysed, and for the great interest he has taken in the whole work.

TRINITY COLLEGE,  
CAMBRIDGE.

CLXVI.—*Tetramethylammonium Hyponitrite and its Decomposition by Heat.*

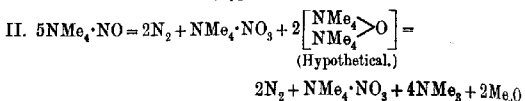
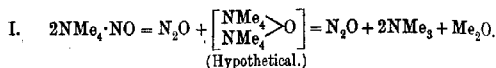
By PRAFULLA CHANDRA RÂY and HEMENDRA KUMAR SEN.

THE decomposition of tetramethylammonium nitrite by heat has been the subject of a previous communication (Proc., 1911, 27, 4). It has been shown that although the salt splits up mainly into its constituents, trimethylamine and methyl nitrite, owing to its stability at a fairly high temperature, the substance ultimately becomes charred, resulting in the formation of various secondary products. We thought it therefore desirable to investigate the thermal decomposition of tetramethylammonium hyponitrite, a salt which is the product of a combination of a strong base with a much "weaker" acid.

*Preparation*:—Pure silver hyponitrite was triturated in a mortar with tetramethylammonium iodide, water being added from time to time. The end-point of the reaction was carefully attained, and the silver iodide filtered off, the filtrate being evaporated in a vacuum over sulphuric acid. It was noticed that the solution, which was practically neutral at first, became more and more alkaline as concentration proceeded, owing to the partial hydrolysis

of the salt. In fact, the presence of free alkali favours the stability of alkali hyponitrites (compare Divers, *Trans.*, 1899, **75**, 113). The crystalline product we obtained was thus a mixture of the hyponitrite with the base tetramethylammonium hydroxide. This circumstance did not interfere with the end we had in view, as tetramethylammonium hydroxide decomposes at a much higher temperature than the hyponitrite; nor could the decomposition products of the hydroxide contaminate those of the hyponitrite in our method of conducting the experiment. The solution of the crystalline mixture gave a yellow precipitate of silver hyponitrite with silver nitrate, and on addition of excess of the latter reagent, a brown precipitate of silver oxide, as might have been expected. That the substance we were dealing with was a tetramethylammonium compound was proved by evaporating a small portion with hydrochloric acid, and converting the hydrochloride into the platonic salt. Two estimations of the percentage of platinum in two distinct preparations gave  $Pt=34.83$  and  $34.95$  respectively, whilst  $(NMe_4Cl)_2PtCl_4$  requires  $Pt=35.1$  per cent.

*Method of Experiment*.:—The substance was introduced into a bulb provided with an elongated stem. A spiral of glass beads, moistened with the liquid which collects on the surface of glacial phosphoric acid, was interposed between the Sprengel pump and the tube. The use of glacial phosphoric acid has much to recommend it, as we have found it of signal service, not only in arresting the amine base, but also the methyl alcohol formed during the decomposition of the quaternary base, whilst it allows all the indifferent gases to pass through, including methyl ether (compare the earlier paper). The bulb was heated in a bath of sulphuric acid. At  $55-60^\circ$  the salt melts to a clear liquid, but the "click" almost persists. At  $75-80^\circ$  gases begin to be evolved, although very slowly, and the evolution becomes regular at about  $110^\circ$ . This goes on until the temperature is allowed to rise to  $140^\circ$ . At this stage the "click" reappears, and remains persistent up to  $190^\circ$ . It was noticed that a slight residue was left in the bulb, which on examination proved to be a mixture of nitrate and carbonate of the tetramethylammonium base. The carbon dioxide had been absorbed by the hydroxide during exposure, and the nitrate was the result of the decomposition of the hyponitrite. This manner of the decomposition of an alkaline hyponitrite is analogous to that of hyponitrous acid itself, as shown by Rây and Ganguli (*Trans.*, 1907, **91**, 1870). Four distinct preparations were undertaken, and subjected to similar treatment, but the behaviour under the action of heat was much the same. It will be shown below that the substance decomposes according to the following equations:



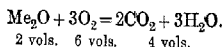
We give here the scheme of a typical analysis of the mixture of gases:

	Volume of gas taken for explosion	...	= 4.7 c.c.
	" " pure oxygen taken	...	= 16.4 "
Therefore total volume before explosion	...	...	= 21.1 "
	Volume after explosion	...	= 17.1 "
" the diminution	...	...	= 4.0 "
	Volume after absorption by NaOH	...	= 12.95 "
" CO <sub>2</sub>	...	...	= 4.15 "
	Volume after absorption by alkaline pyrogallol	...	= 2.35 "
" oxygen unused	...	...	= 10.6 "

The residual 2.35 c.c., or practically 2.4 c.c., of gas were found to be pure nitrogen.

A fresh portion of the gas was next analysed as follows: A drop of concentrated sulphuric acid was introduced into the eudiometer, when the mercury at once began to rise. After the absorption was complete, a reading was taken, which gave the volume of methyl ether, and the volume thus ascertained agreed well with that deduced from explosion. The eudiometer was inverted over water, and shaken vigorously. The water-level began to rise slowly, a characteristic behaviour in the case of nitrous oxide. The residue was found to be pure nitrogen. The proportion of nitrogen to nitrous oxide in almost all the experiments was 1:1.5.

The gas, after explosion and absorption of carbon dioxide and oxygen, was found to be pure nitrogen, inasmuch as the nitrous oxide took part in the explosion and yielded up its oxygen, being thereby reduced to its own volume of nitrogen. If the explosive gas be taken to be methyl ether, the following volume relations should exist:



That is, eight volumes of mixed gases ought to give four volumes; in other words, there should be a shrinkage of half the volume, which is the same thing as saying that the volume of carbon dioxide produced must be equal to the shrinkage. On comparing the

experiments, this will be found to be actually the case. Since 4.2 c.c. of carbon dioxide were formed, half its volume, namely, 2.1 c.c., must have been methyl ether, and the remaining 2.6 c.c. of the total 4.7 c.c., nitrogen and nitrous oxide. The actual experiment gave 2.4 c.c. of these gases, a difference which is evidently within the limits of experimental error. On comparing the data, it will be found that 10.6 c.c. of oxygen remained unused; hence the amount of used oxygen was  $16.4 - 10.6 = 5.8$  c.c. Now, in the combustion of 2.1 c.c. of methyl ether, 6.3 c.c. of external oxygen is necessary, of which 5.8 c.c. were supplied by the pure oxygen, and the rest, 0.5 c.c., by nitrous oxide. This is also a way of indirectly measuring the volume of nitrous oxide present, since nitrous oxide contains half its volume of oxygen. Thus the proportion of nitrogen to nitrous oxide in the particular experiment was as 1.6:1. It may be pointed out here that the qualitative and practically the quantitative test for methyl ether with the help of a drop of sulphuric acid or two may well be adopted in gas analysis in the absence of basic gases. The absorption of unsaturated hydrocarbons, for example, ethylene, by concentrated sulphuric acid is at the ordinary temperature very slow, and effective only with fuming sulphuric acid.

The decomposition therefore takes place according to the equations given above. They explain the simultaneous formation of nitrogen and nitrous oxide. Of course, how far one reaction proceeds in preference to the other it is difficult to say, and possibly this varies according to the nature of the experiment. In our experiments, however, we found the reactions proceeding side by side, since the volumes of ether and nitrogen plus nitrous oxide were approximately found to be equal, as required by the above reactions.

Something remains to be said about the concomitant impurity of the hyponitrite, namely, the hydroxide. The decomposition of tetramethylammonium hydroxide has been studied by Hofmann, and later on by Schmidt (*Annalen*, 1892, 267, 263), and confirmed by ourselves. The products are trimethylamine and methyl alcohol in equivalent proportions:



The formation of methyl alcohol by the decomposition of the substance we obtained was qualitatively proved by heating a small quantity in a bulb tube with salicylic acid, when the characteristic odour of oil of wintergreen was distinctly perceptible. The methyl alcohol in our experiments was arrested by the phosphoric acid spiral along with the tertiary amine. Blank experiments were made with pure methyl alcohol. A small sealed bulb containing

the alcohol was introduced into a bulb tube connected with the phosphoric acid spiral. After the system was exhausted, the alcohol bulb was broken by a sudden jerk. The alcohol at once rushed into the spiral, but none into the collecting tube.

The amine arrested in the spiral during the experiments was washed out, treated with alkali hydroxide, and subjected to distillation, the distillate being caught in hydrochloric acid. The solution was evaporated to dryness, and the hydrochloride converted into the platonic salt, and analysed. (Found, Pt=36.85. Calc., Pt=36.85 per cent.)

It will thus be seen that pure trimethylamine, as demanded by the above equations, was given off.

From the foregoing investigations it is thus established that the products of thermal decomposition of tetramethylammonium hyponitrite are nitrogen monoxide, nitrogen, methyl ether, and trimethylamine; at the same time a small quantity of the hyponitrite is converted into nitrate.

CHEMICAL LABORATORY,  
PRESIDENCY COLLEGE, CALCUTTA.

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CLXVII.—*Nitrites of the Alkylammonium Bases: Ethylammonium Nitrite, Dimethylammonium Nitrite, and Trimethylammonium Nitrite.*

By PRAFULLA CHANDRA RÂY and JITENDRA NATH RAKSHIT.

*Ethylammonium Nitrite.*

THE method adopted for the preparation of this salt was exactly the same as that of its lower homologue, namely, double decomposition between mercuric nitrite and ethylamine or interaction between the amine hydrochloride and silver nitrite (compare this vol. p. 1016). The first method gave, however, an altogether unexpected result in that we obtained, not only diethylmercurammonium nitrite, but, under favourable conditions, diethyltrimercurammonium nitrite, which will form the subject of a separate communication. The filtrate from these mercury compounds was subjected to distillation; the distillate gave copious precipitate of iodoform on treatment with iodine and sodium hydroxide, proving that ethylammonium nitrite was formed, which, during distillation, was decomposed into ethyl alcohol and nitrogen.

As, however, the various primary, secondary, and tertiary amines and their hydrochlorides we had to deal with are not available in this country, we had to undertake their preparation in each instance and test their freedom from impurities, especially ammonia. Our first attempt to prepare pure ethylamine by the reduction of acetonitrile by Mendius' reaction, as improved by Siersch (*Annalen*, 867, 144, 139), gave undesirable results. Very considerable quantities of ammonium chloride were simultaneously formed, and the mixture, when extracted with absolute alcohol or a mixture of ether and alcohol, was contaminated with notable proportions of the latter. Ladenburg's modification of the method (reduction by sodium in alcohol) gave a far better yield. In connexion with this we may mention here that the extraction of the amine hydrochloride from a mixture containing sal ammoniac is only successful by Winkler's process (*Annalen*, 1855, 93, 324) when the former is present in considerable excess. Analysis of the platinichloride showed that the base was pure. (Found, Pt=39.03. Calc., Pt=38.93 per cent.)

The filtrate from the interaction of amine hydrochloride and silver nitrite was evaporated in a vacuum as usual. The product obtained, however, was a heavy liquid, which, on immersion in a mixture of salt and ice, could not be solidified. It is remarkable that whilst methylammonium nitrite is a crystalline solid (m. p. 50° approx.), its higher homologue is a liquid. Two distinct preparations were undertaken, the analyses of which are given below:

I. 0.1348 gave 0.1298 CO<sub>2</sub> and 0.1014 H<sub>2</sub>O. C=26.26; H=8.35.  
0.1770 „ 43.5 c.c. N<sub>2</sub> at 30° and 760 mm. N=27.70.

II. 0.2450 gave 0.2286 CO<sub>2</sub> and 0.1962 H<sub>2</sub>O. C=25.43; H=8.89.  
C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>N<sub>2</sub> requires C=26.09; H=8.69; N=30.43 per cent.

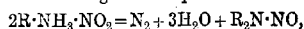
As the nitrogen was collected in a Schiff's azotometer, the vapour tension was taken to be half the tension of aqueous vapour at that temperature.

The low percentage of nitrogen is accounted for by the fact that during combustion while the air in the tube was being expelled by the current of carbon dioxide, minute bubbles of gas were continuously given off from the liquid nitrite; thus, not only was it a difficult matter to ascertain when the tube was free from air, but traces of the nitrogen were carried away. Estimation of nitrogen by the "Crum Frankland" and "Urea" processes gave the percentage in the two preparations as 15.6 and 15.1 respectively, that is, half the total amount of nitrogen.

*Ethylammonium nitrite* is a yellow liquid, having a specific

gravity of 1.125 (approx.) at 39° compared with water at the same temperature. Even at the ordinary temperature of the laboratory (23° to 30°) it slowly dissociates. It is soluble in chloroform or alcohol (90 per cent.), and almost insoluble in ether.

*Decomposition by Heat*:—In the vacuum of the Sprengel pump ethylammonium nitrite slowly decomposes, even at the ordinary temperature; on raising the temperature, the rate of decomposition increases; at 60° it is regular, and at this temperature it is conveniently decomposed. Finally, the temperature was raised to 100° until the "click" became persistent. The small quantity of the liquid which distilled over contained water and ethyl alcohol; the latter being tested by the iodoform reaction. The distillate also responded to the nitroso-reaction. Minute, oily drops, which gave the nitroso-reaction, also condensed in the upper cooler part of the tube. The formation of a nitroso-derivative by the distillation of a primary ammonium nitrite is, no doubt, striking. Linnemann also noticed the simultaneous formation of isopropyl alcohol and nitrosodipropylamine by heating the aqueous solution of propylammonium nitrite (*Annalen*, 1872, 161, 47). Accepting Linnemann's view, we provisionally explain the formation of nitrosoalkylamine according to the equation:



where  $R$  represents an alkyl radicle. It may be mentioned here that in the case of methylammonium nitrite also a corresponding nitrosoamine is obtained. The gaseous mixture consisted of nitrogen and nitric oxide, with traces of free ethylamine.

#### *Dimethylammonium Nitrite.*

This compound, prepared as before by the interaction of silver nitrite and the corresponding amine hydrochloride\* and evaporation in a vacuum of the filtrate, was a pale yellow, transparent liquid:

0.3389 gave 0.3716  $CO_2$  and 0.2763  $H_2O$ .  $C = 25.39$ ;  $H = 9.08$ .

0.1685 „ 42.0 c.c.  $N_2$  at 29° and 760 mm.  $N = 28.30$ .

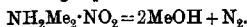
$C_2H_5O_2N_2$  requires  $C = 26.09$ ;  $H = 8.69$ ;  $N = 30.43$  per cent.

The result for nitrogen is rather low, as in the case of the previous salt, for reasons assigned thereunder. When estimated by the "Crum Frankland" and "Urea" processes, the percentage was 14.75, that is, nearly half the total amount.

*Decomposition by Heat*:—The salt decomposes slightly at the

\* The platinum salt of two distinct preparations gave  $Pt = 89.15$  and  $39.03$ . Calc.,  $Pt = 88.93$  per cent.

ordinary temperature in a vacuum; at 60° the decomposition is fairly regular; the gaseous products are nitrogen and a trace of free dimethylamine. In the distillate, methyl alcohol was also detected. Evidently the nitrogen and methyl alcohol were formed according to the following equation:



In some cases a small quantity of nitric oxide was detected. The main portion of the salt was, however, converted into nitroso-dimethylamine, which gave Liebermann's nitroso-reaction, and its boiling point was found to be 144° (approx.)\* by Jones' method (Trans., 1878, **33**, 175). There was a slight solid residue, which was not decomposed at 100°, and this proved to be a nitrate. Dimethylammonium nitrite is stable at 21° to 23°. When first prepared, in January last, the laboratory temperature was 21°. After an interval of two months, during which period the temperature of the laboratory gradually increased to 30°, a portion of the substance was converted into the nitroso-compound. An estimation of "nitritic" nitrogen by the "Urea" process showed that 76.73 per cent. was real nitrite. It may be pointed out here that the nitroso-compound does not respond to the "Urea" test.

#### *Trimethylammonium Nitrite.*

The trimethylamine which was required for the purpose was prepared by the dry distillation of tetramethylammonium hydroxide in a current of dry hydrogen (Schmidt, *Annalen*, 1892, 267, 263). Analysis of the platinichloride showed that the base was pure. (Found, Pt=36.72. Calc., Pt=36.85 per cent.)

The method of preparation of the nitrite was exactly the same as in the preceding cases. The salt was obtained in beautiful pale green crystals. It was extremely deliquescent:

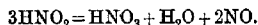
0.1275 gave 0.1496 CO<sub>2</sub> and 0.1077 H<sub>2</sub>O. C=32.00; H=9.38.

0.0818 " 9.8 c.c. N<sub>2</sub> ("nitritic") (moist) at 23° and 760 mm.

N ("nitritic")=13.44.

C<sub>3</sub>H<sub>10</sub>O<sub>2</sub>N<sub>2</sub> requires C=33.98; H=9.39; N=13.20 per cent.

*Decomposition by Heat*:—The salt slowly and continuously dissociates into trimethylamine and nitrous acid, even at the ordinary temperature. The nitrous acid in turn breaks up according to the equation:



The nitric acid thus generated combines with a portion of the

\* The substance contained a trace of moisture which had the effect of lowering the boiling point.

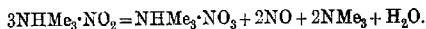


free amine (the product of dissociation), resulting in the formation of trimethylammonium nitrate. It is for this reason that a perfect vacuum cannot be obtained when a tube containing the salt is attached to the Sprengel pump. Minute bubbles are given off, which interfere with the persistency of the "click." When the temperature is slowly raised, the rate of decomposition increases. At 55° the salt melts to a pale green, viscous liquid, from which bubbles continually escape. As water is one of the products of decomposition, the melting point of the salt cannot be accurately determined. On withdrawing the bath, the molten substance solidifies *en masse* to its original crystalline structure and green colour. The decomposition is effected conveniently at 100°. During this stage minute drops of a colourless liquid condensed in the upper part of the tube, which, after the completion of the decomposition and removal of the bath, solidified to a thin, white layer. An appreciable quantity of residue was left in the tube.

The gaseous mixture which was collected consisted of equal volumes of trimethylamine and nitric oxide, with traces of nitrogen. That it was trimethylamine was proved by its absorption by hydrochloric acid and the conversion of the hydrochloride into the platonic salt. (Found, Pt=37.37. Calc., Pt=36.85 per cent.)

The white, crystalline residue which was not decomposed at 100° was shown by analysis to consist of slightly impure trimethylammonium nitrate. (Found, C=26.20; H=8.07; N=21.90. Calc., C=29.50; H=8.19; N=23.10 per cent.)

The decomposition evidently proceeds according to the equation:



A sample of trimethylammonium nitrite prepared in December last (the temperature of the laboratory being 21°) was found on examination in the middle of March (temp. 30°) to consist of 51 per cent. of nitrite and 49 per cent. of nitrate.

*Concluding Remarks on the Alkylammonium Nitrites:*—It will be evident from the present investigation that, not only the primary, but the secondary and tertiary amines also yield the corresponding nitrites. The order of stability of these salts is what might have been expected from the heat of neutralisation of these organic bases with hydrochloric acid. Thus, methylamine and ethylamine evolve 26,000 calories in round numbers, whilst dimethylamine and trimethylamine evolve 23,000 and 17,000 calories respectively. The primary ammonium nitrites have been found to be the most stable, and trimethylammonium nitrite the least; the latter, in fact, undergoes complete dissociation into nitrous acid and trimethylamine. All ammonium nitrites, however, dis-

sociate more or less, even at the ordinary temperature, and if these nitrites are kept in a desiccator in an open dish they slowly find their way into the sulphuric acid, being ultimately completely absorbed by this reagent. In a vacuum desiccator this absorption takes place more rapidly.

CHEMICAL LABORATORY,  
PRESIDENCY COLLEGE, CALCUTTA.

CLXVIII.—*Nitrites of the Benzylammonium Series.*  
*Benzylammonium Nitrite and Dibenzylammonium*  
*Nitrite and their Sublimation and Decomposition*  
*by Heat.*

By PRAFULLA CHANDRA RÂY and RASIK LAL DATTA.

*Benzylammonium Nitrite.*

IN continuation of the work on the aliphatic amine nitrites, we were led to the study of the nitrites of the benzylammonium series, and it appears that the nitrites of this series are more stable than the corresponding nitrites of the aliphatic amines. The first of the series, namely, monobenzylammonium nitrite, was prepared as usual by the double decomposition of silver nitrite and monobenzylamine hydrochloride and evaporation of the resulting solution in a vacuum over sulphuric acid. Monobenzylamine hydrochloride was prepared according to Mason's method (Trans., 1893, 63, 1311) by the action of alcoholic ammonia on benzyl chloride, which gave very satisfactory results.

The salt as prepared in the above manner is of a pale yellow colour, and consists of crystalline plates. It is hygroscopic and stable. It is soluble in alcohol, ether, or benzene. Unlike the alkylammonium nitrites, it does not decompose into its constituents, and even undergoes sublimation in a vacuum. It is very remarkable that an amine nitrite with a very heavy group,  $C_6H_5 \cdot CH_2$ , is more stable than amine nitrites with such lighter groups as methyl, ethyl, etc.; on the other hand, ammonium nitrite in which no atom of hydrogen is substituted is more stable than the alkyl-substituted ammonium nitrites, so much so that the former can be sublimed, whilst the latter have no tendency to sublime, and are easily decomposable. In the case of benzyl-

ammonium nitrite it is the substitution of the phenyl in the methyl group that determines its stability and subliming property. As a rule, aromatic compounds are especially endowed with such a property.

Analysis of benzylammonium nitrite gave the following results:

0.3614 gave 0.7002  $\text{CO}_2$  and 0.2164  $\text{H}_2\text{O}$ .  $\text{C}=52.85$ ;  $\text{H}=6.65$ .

0.1216 „ 19.7 c.c.  $\text{N}_2$  (moist) at  $30^\circ$  and 760 mm.  $\text{N}=17.94$ .

$\text{C}_7\text{H}_{10}\text{O}_2\text{N}_2$  requires  $\text{C}=54.54$ ;  $\text{H}=6.49$ ;  $\text{N}=18.18$  per cent.

The "nitritic" nitrogen, as estimated by the "Crum Frankland" and "Urea" methods, gave 8.86 per cent. instead of 9.09, that is, half the total nitrogen required by theory.

*Sublimation and Decomposition by Heat*:—When the salt was heated in a Sprengel vacuum (compare Rây, Trans., 1909, 95, 345) it began to sublime at  $80^\circ$ , and on maintaining the temperature of the bath between  $80^\circ$  and  $85^\circ$ , practically the whole of the substance sublimed, and was deposited on the upper and cooler parts of the tube in beautiful white, stellate clusters of crystals. It is noteworthy that whilst the salt as originally prepared has a pale yellow tint, the sublimed crystals are colourless. An estimation of "nitritic" nitrogen of the sublimate gave 9.07 per cent. instead of 9.09 as required by theory. In this connexion, an interesting fact was discovered. The tube containing the sublimate was kept in a vacuum in an open bottle over sulphuric acid; on the next day, the bottle containing the tube was found to be lined with white clouds of the salt. This proves that the substance (once sublimed) very slowly sublimes in a vacuum at the ordinary temperature ( $30^\circ$ ).

If, instead of keeping the temperature between  $80^\circ$  and  $85^\circ$ , the bath is heated to a higher temperature, the salt melts, and begins to decompose into benzyl alcohol and nitrogen according to the equation:



a decomposition which takes place at once when the hydrochloride is directly treated with nascent nitrous acid (sodium nitrite and sulphuric acid).

The benzyl alcohol was recognised by its odour and by conversion into benzaldehyde and benzoic acid by nitric acid and alkaline permanganate respectively. The nitrogen was found to be free from nitric oxide. A quantitative experiment gave  $\text{N}=14.45$ , instead of 15.18 per cent., as required by theory. The deficit was due to a small part of the substance subliming unchanged, and being carried off as fine dust into the "fall-tube" and thus escaping decomposition.

*Dibenzylammonium Nitrite.*

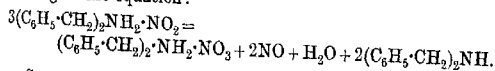
The dibenzylamine hydrochloride was prepared simultaneously with monobenzylamine hydrochloride, according to Mason's method, since both are formed at the same time by the action of alcoholic ammonia on benzyl chloride. Double decomposition between the amine hydrochloride in aqueous solution and silver nitrite gave the corresponding amine nitrite. The solution was evaporated in a vacuum over sulphuric acid, and the salt was obtained in white scales. It was not deliquescent, and was somewhat sparingly soluble in water, but readily soluble in ether or alcohol:

0.1629 gave 0.4020  $\text{CO}_2$  and 0.0958  $\text{H}_2\text{O}$ .  $\text{C} = 67.30$ ;  $\text{H} = 6.54$ .

Found:  $\text{N}$  (nitritic) = 6.15.

$\text{C}_{14}\text{H}_{16}\text{O}_2\text{N}_2$  requires  $\text{C} = 68.85$ ;  $\text{H} = 6.56$ ;  $\text{N} = 5.74$  per cent.

*Sublimation and Decomposition by Heat:*—The substance was heated in the Sprengel vacuum, and it simultaneously melted and sublimed at about  $110^\circ$ . On maintaining the temperature at this point for some time, the molten mass disappeared, a white, crystalline sublimate was deposited in the cooler parts of the tube, and a small quantity of gas was collected, which was found to be almost pure nitric oxide. A thin but distinct layer of a crystalline solid was left behind. It was found on examination to be dibenzylamine nitrate. Viscid, oily drops were also deposited just below the sublimate. This liquid turned red litmus blue. Evidently it was dibenzylamine, which boils at  $300^\circ$  under the ordinary pressure, but at about  $180^\circ$  in a vacuum. The sublimate was found to be dibenzylamine nitrite. Traces also were carried off into the "fall tube," which was washed with alcohol, and the solution responded to the test for a nitrite. The major portion of the salt thus sublimed unchanged; a small fraction undergoes decomposition according to the equation:



CHEMICAL LABORATORY,  
PRESIDENT COLLEGE, CALCUTTA.

CLXIX.—*The Density of Liquid Sucrose and of its Solutions in Water.*

By FREDERIK SCHWERS.

THE densities of aqueous solutions of sucrose have been carefully determined by Gerlach (*Dingl. polyt. J.*, 1864, **172**, 35) for seven different concentrations and between 0° and 100°. With the object of continuing my previous researches on binary mixtures (*Bull. Acad. roy. Belg.*, 1908, 814; *Rec. trav. chim.*, 1909, **28**, 261; *J. Chim. phys.*, 1911, **9**, 15), and calculating the variations undergone by the volume-contractions with the temperature, it was first of all necessary to obtain data on the density of sucrose in the liquid and superfused state. On its passage into solution, sucrose, like any other solid, occupies the volume it would have in the liquid state at the temperature of the dissolution; Wulff (*Zeitsch. f. die ges. Rübenzuckerindustrie*, 1887, **37**, 918) has already called attention to this point. I could not find, however, any such determinations in the extensive literature relating to this subject; in view of the great number of chemists who have studied sucrose, this can only be explained by the great experimental difficulties of determinations of this kind.

Several investigators have tried to obtain an approximate value by means of extrapolation from the density curve of aqueous sucrose solutions. This value is between 1.5549 and 1.56165\*; but we cannot place much reliance in these numbers, owing to the fact, to which Plato (*Zeitsch. f. die ges. Rübenzuckerindustrie*, 1900, **50**, 1098) has already called attention, that it is impossible to prepare solutions stronger than 76 per cent., and that an extrapolation, which extends over nearly 25 per cent., can only give a rough approximation. It may be added that it is impossible to find out in this way the expansion-coefficient of liquid sucrose.

The greatest experimental difficulties were to melt the sucrose without the slightest decomposition, and to maintain it in the super-fused state for sufficient time to make all the determinations.

According to Braconnet (*Ann. Chim. Phys.*, 1821, [ii], **16**, 427), sucrose melts to a clear liquid when carefully heated in the neighbourhood of its melting point, but in spite of careful purification of the sucrose by fractional precipitation of the aqueous solution with ethyl alcohol, and very slow heating in an oil-bath, I could

See the complete data on this subject in *Die Chemie der Zuckerarten* by E. von Lippmann, 1904, 3rd ed. Braunschweig.

not avoid a slight decomposition whenever the sucrose was exposed to air.

After a long series of unsuccessful attempts, I at last secured the desired result by melting finely pulverised sucrose under a liquid. This mode of procedure avoids charring due to superheating, diminishes oxidation by contact with air, and, moreover, favours retention in the liquid state. The liquid used must be without chemical or physical action on sucrose; it must be non-oxidising, and possess a boiling point above the melting point of saccharose. Of all the liquids tried, I found liquid paraffin the most convenient (b. p. about  $190^{\circ}$ ).

The pycnometer used was a small flask of Jena-glass of about 50 c.c. capacity, the neck of which had been drawn out and marked. The powdered sugar was first introduced and weighed, the flask filled with paraffin, and carefully heated until the melting point was reached. The apparatus was then placed in a thermostat, which was kept very constant, and the paraffin adjusted to the mark. The weight was taken when the apparatus had reached the temperature of the balance room. The density of the paraffin used was previously determined in the same apparatus, the volume of which was ascertained by filling with water. All the experiments were made at the same temperature in order to eliminate errors due to the imperfections of the method. Needless to say, all the weighings were reduced to a vacuum—an important correction in the case of such large quantities.

By this method I was able to determine the density of sucrose down to  $-15^{\circ}$ , without crystallisation; the sugar becomes more and more viscous, and ultimately hard like glass, which we may also regard as being in the superfused state.

The densities, compared with water at  $4^{\circ}$ , are as follows:

$t^{\circ}$ .	$d^{\circ}/4^{\circ}$ .	$t^{\circ}$ .	$d^{\circ}/4^{\circ}$ .
-14.55	1.51966	45.85	1.50605
0.00	1.51915	59.00	1.49812
14.00	1.51756	77.85	1.48493
20.55	1.51663	101.55	1.46790
33.75	1.51245	114.70	1.45846

Or, taking the volume at  $0^{\circ}$  as unity, the volumes at the other temperatures are as follows:

$t^{\circ}$ .	Vol. $t^{\circ}/0^{\circ}$ .	Variation per degree.	$t^{\circ}$ .	Vol. $t^{\circ}/0^{\circ}$ .	Variation per degree.
-14.55	0.99966	0.000023	45.85	1.00870	0.000406
0.00	1.00000	0.000075	59.00	1.01404	0.000478
14.00	1.00105	0.000093	77.85	1.02305	0.000500
20.55	1.00166	0.000210	101.55	1.03490	0.000510
33.75	1.00443	0.000353	114.70	1.04161	

Between  $35^{\circ}$  and  $115^{\circ}$  the dilatation is almost regular (see

diagram II), and approximately four times that of solid sucrose according to Joule and Playfair (*Quart. Journ. Chem. Soc.*, 1848, 1, 121), who give 0.0001116 between 0° and 100°. Below this temperature, however, it diminishes rapidly, although regularly; between 15° and 20° it attains the value of that of solid sucrose, and between 0° and -15° it is very much less.

The rapid bending of the curve led me first to suppose the existence of a real density-maximum, as in the case of water: but after a large number of very careful experiments, I came to the conclusion that the curve is as shown in the figure; so that, if there is really a density-maximum, it has not been reached at the temperature of -15°. Unfortunately, the method used does not permit investigations at lower temperatures with the same degree of exactness. The reservoir above the mark ought to be much larger to allow the expansion of the paraffin, owing to the fact that the weighing must be done at the ordinary temperature, and it would be difficult to avoid slight loss by evaporation; moreover, there is a practical obstacle, due to the solidification of the paraffin.

The calculation of an analytical form of the curve *V*, would involve much work, owing to its sinuosity, without giving any explanation of the particular form of the curve; the nature of the phenomena is sufficiently well indicated by the graphic representation.

The experiments were not continued beyond 115°, because it is more difficult to obtain the same degree of accuracy, and also because the maintenance during several hours at a temperature so near to the melting point initiates charring and decomposition. It appears quite certain that the continuation of the curve approximates to a straight line.

It is between 35° and 40° that the great change in the dilatation occurs. It may be interesting to point out that superfused sugar possesses down to 38° a certain fluidity, so that it is still possible to draw it out in threads, whereby crystallisation takes place, as was first observed by Dumas. Below this temperature, the viscosity becomes so great that the substance has the appearance of a solid.

For liquids with non-associated molecules only, the variations of the volume with the temperature may be represented on a diagram by a straight line. With liquids forming physical aggregates (which is the general case), the volume-curve becomes more nearly parallel to the abscissa with decreasing temperature at a point which is peculiar to the liquid in question.

In a previous paper (*J. Chim. phys.*, 1911, 9, 72) I have shown that the hypothesis of De Heen, elaborated afterwards by Van Laar, gives the best explanation of the facts. We have to consider

the volume-changes of a liquid by heating as the result of two opposite actions: the heat gives more energy to the molecules, and increases the volume, but, on the other hand, the partial depolymerisation—or physical dissociation—of the aggregates produces a decrease of volume.

Water has been, so far, the only liquid known for which the second of these actions exceeds the first (between  $0^{\circ}$  and  $4^{\circ}$ ); as is now seen, liquid sucrose approaches very nearly to water in this respect, and is perhaps quite similar at lower temperatures. As I have already pointed out in the above-mentioned paper, the presence of a real density-maximum is not a sufficient reason for placing a liquid in a special class; this maximum shown by water is only an external manifestation—in a higher degree—of a property which is common to all associated liquids.

It appears from observations on a large number of liquids that the presence of hydroxyl groups in the molecule is particularly favourable to physical association; no wonder that sugar (with its large number of these groups) possesses more associating power than the alcohols.

If similarity in the form of the  $V_r$ -curve permits us to assume a similar state of polymerisation, it would appear from this study that water possesses a much higher degree of association than we have hitherto believed—higher than that of sucrose, of which the smallest molecule has ten hydroxyl groups.

#### *Aqueous Solutions of Sucrose.*

As already mentioned, it was of interest to determine the departure shown by the different water-sucrose mixtures from the theoretical density, as calculated from the well-known formula:

$$d_v = \frac{p_1 + p_2}{\frac{p_1}{d_1} + \frac{p_2}{d_2}} \quad \text{or} \quad d_v = \frac{p_1 + p_2}{v_1 + v_2}.$$

If we calculate from the density of *solid* sucrose (which is approximately 1.59), we find a slight contraction up to 63 per cent. of sucrose, and a dilatation for solutions of higher concentration. Plato (*Zeitsch. f. die ges. Rübenzuckerindustrie*, 1900, 50, 1098), however, admitted that the volume contraction must be calculated from the value of *liquid* sucrose. Using the number he obtained by extrapolation from aqueous solutions (1.55626 at  $17.5^{\circ}$ ), he concluded that all the solutions exhibit contraction, which is a maximum (1.37 per cent.) at a concentration of nearly 60 per cent. of sucrose. It might be first objected that, for our purpose, the method is not sufficiently accurate to determine the dilatation-



coefficient of liquid sucrose, which is quite necessary to calculate the volume-contraction of the solutions up to  $100^{\circ}$ . As, on the other hand, it has just been shown that experiment gives a density quite different (less than 1.52) from the extrapolated value (1.55 to 1.56), it is clear that experimental verification was necessary. It follows that the volume-contraction is much more pronounced than would appear from Plato's calculations. In the following tables are given the calculations I have made from Gerlach's experimental data (*loc. cit.*). The numbers for density  $d$  reproduced in the first column are from experimental observation, and not the interpolated values; I have given these, as Gerlach did, to six places of decimals, although I think that the last place might, for our purpose, be omitted. The densities are referred to water at  $17.5^{\circ}=1$ ; it was needless to transform those in the values  $d\ t^{\circ}/4^{\circ}$ , because the final result  $C_v$  is the same in both cases. As in the tables already published,  $d$  is the observed, and  $d_v$  the theoretical density; the volume contraction is readily calculated from the formula  $1-d_v/d$ .

*Sucrose: 10 per cent. + Water: 90 per cent.*

$t^{\circ}$	$d\ t^{\circ}/17.5^{\circ}$	$d_v$	$d_v/d$	$C_v$
0.9	1.041792	1.036112	0.99455	0.545
9.2	1.041356	1.036176	0.99502	0.498
12.4	1.040948	1.035955	0.99520	0.480
15.3	1.040521	1.035571	0.99524	0.476
17.5	1.040104	1.035366	0.99544	0.456
25.5	1.038037	1.033772	0.99589	0.411
32.4	1.035961	1.031895	0.99607	0.393
43.3	1.031848	1.028091	0.99636	0.364
52.6	1.027764	1.024150	0.99658	0.342
60.9	1.023710	1.020136	0.99661	0.349
68.7	1.019686	1.015822	0.99621	0.379
75.9	1.015691	1.011632	0.99605	0.385
82.4	1.011725	1.007666	0.99599	0.401
88.5	1.007788	1.003883	0.99607	0.393
94.3	1.003880	1.000224	0.99637	0.363
99.9	1.000000	0.996650	0.99665	0.335

*Sucrose: 20 per cent. + Water: 80 per cent.*

$t^{\circ}$	$d\ t^{\circ}/17.5^{\circ}$	$d_v$	$d_v/d$	$C_v$
5.9	1.085477	1.074283	0.98969	0.031
17.5	1.083234	1.073324	0.99085	0.015
31.6	1.078779	1.070028	0.99188	0.012
42.6	1.074356	1.065889	0.99212	0.083
52.0	1.069985	1.062065	0.99262	0.738
60.8	1.065605	1.057635	0.99252	0.748
68.9	1.061278	1.053153	0.99234	0.766
76.3	1.056982	1.048619	0.99209	0.791
89.3	1.048482	1.040460	0.99235	0.765
95.6	1.044278	1.036499	0.99255	0.745

*Sucrose: 30 per cent. + Water: 70 per cent.*

$t^{\circ}$	$d^{\circ}P/17.5^{\circ}$	$d_m$	$d_d d.$	$C_p$
9.2	1.131996	1.115026	0.98501	1.499
17.5	1.129586	1.114169	0.98635	1.365
31.2	1.124800	1.110986	0.98772	1.228
42.4	1.120048	1.106745	0.98812	1.188
52.0	1.115330	1.102421	0.98842	1.158
61.0	1.110846	1.097835	0.98847	1.153
69.3	1.105995	1.092933	0.98819	1.181
77.2	1.101377	1.088311	0.98813	1.187
84.5	1.096792	1.083684	0.98805	1.195
91.3	1.092240	1.079389	0.98823	1.177
97.9	1.087721	1.075070	0.98837	1.163

*Sucrose: 40 per cent. + Water: 60 per cent.*

-0.18	1.134531	1.159245	0.97865	2.135
9.8	1.131945	1.159102	0.98067	1.933
17.5	1.179358	1.158252	0.98210	1.790
30.9	1.174222	1.155094	0.98371	1.629
42.0	1.169121	1.150642	0.98420	1.580
52.0	1.164056	1.146050	0.98453	1.547
61.0	1.159026	1.141318	0.98472	1.528
69.6	1.154032	1.136145	0.98450	1.550
78.0	1.149073	1.131149	0.98440	1.560
85.9	1.144150	1.126074	0.98420	1.580
93.3	1.139261	1.121392	0.98432	1.563

*Sucrose: 50 per cent. + Water: 50 per cent.*

1.96	1.238293	1.207098	0.97489	2.511
17.5	1.232748	1.206054	0.97834	2.166
30.4	1.227241	1.202935	0.98019	1.981
41.9	1.221771	1.198184	0.98089	1.931
52.2	1.216339	1.193172	0.98095	1.905
61.8	1.210945	1.187974	0.98103	1.897
70.9	1.205589	1.182117	0.98053	1.947
79.5	1.200269	1.177134	0.98072	1.928
87.6	1.194986	1.171829	0.98062	1.938
95.3	1.189740	1.166975	0.98087	1.913

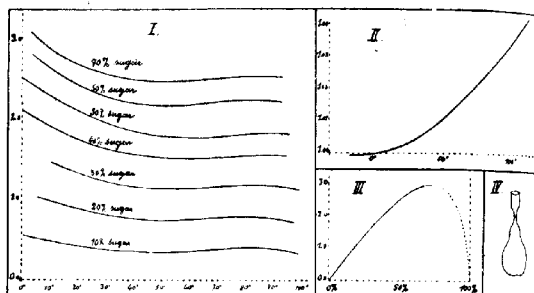
*Sucrose: 60 per cent. + Water: 40 per cent.*

3.1	1.295890	1.259105	0.97161	2.339
17.5	1.289952	1.257773	0.97505	2.495
30.7	1.284054	1.254806	0.97722	2.278
42.4	1.278197	1.249386	0.97741	2.259
52.9	1.272379	1.244075	0.97768	2.232
62.9	1.266600	1.238467	0.97779	2.221
72.5	1.260961	1.232593	0.97758	2.242
81.5	1.255161	1.226804	0.97741	2.259
90.1	1.249500	1.221396	0.97751	2.249
98.4	1.243877	1.215669	0.97732	2.268

*Sucrose: 70 per cent. + Water: 30 per cent.*

$t$ .	$d_t/17.5^\circ$ .	$d_m$ .	$d_t/d_m$ .	$C_m$ .
9.3	1.357518	1.315594	0.96912	3.088
17.5	1.351168	1.314240	0.97267	2.733
31.0	1.344860	1.310629	0.97455	2.545
43.8	1.338594	1.304781	0.97474	2.526
55.1	1.332370	1.298785	0.97478	2.522
65.5	1.326188	1.292790	0.97482	2.518
75.0	1.320046	1.286652	0.97470	2.530
84.4	1.313946	1.280357	0.97444	2.556
93.4	1.307887	1.274543	0.97450	2.550

The diagram on which these values are plotted shows—better than the numbers—the variations of  $C_m$  for each mixture of sucrose and water. The general form of the curves (they are very similar



- I. *Abscissae: Temperature.*  
*Ordinates: Contraction in percentage of the initial volume.*
- II. *Abscissae: Temperature.*  
*Ordinates: Volume of liquid sucrose (volume at  $0^\circ = 1$ ).*
- III. *Abscissae: Weight per cent. of sugar.*  
*Ordinates: Volume contraction (at  $0^\circ$ ) in percentage of the initial volume.*
- IV. *Pycnometer used for the density determinations.*

for all the concentrations) shows a diminution of the contraction up to nearly  $50^\circ$ ; then each curve becomes parallel to the abscissa, and an increase of contraction takes place with a maximum at about  $80^\circ$ . After the bend, the curve descends again at higher temperatures.

This behaviour is analogous to that previously observed in other binary mixtures, and especially described in my papers on the aqueous solutions of the different alcohols. By comparing the forms of the contraction curves of mixtures of water with ethyl alcohol, glycol, and glycerol, I observed that the bends become more marked

as the number of hydroxyl groups increases; on the other hand, that the maximum occurs at higher temperatures as the boiling points of the alcohol rise.

In the case of sucrose, the incurvation is rather pronounced, but not in proportion to the large number of hydroxyl groups; the form of the curves is not very different from that of the system glycerol + water, and the maximum occurs at nearly the same temperature (about 80°).

Similar remarks apply to other properties. For example:

(1) If we consider, for the pure liquids, the portion of the  $V_r$ -curve which is nearly a straight line, we see that the volume change for 1° is approximately as follows (the volume at 0° being = 1):

Ethyl alcohol .....	0.0013
Glycol .....	0.00085
Glycerol .....	0.0006

For sucrose, the value 0.0005 (approx.) was found, which approaches very closely to the number for glycerol. It may here be recalled, as a general rule, that the largest differences in physical properties occur in organic compounds with fewest carbon-atoms, and that these differences diminish as the carbon-chain lengthens.

(2) If we consider, at the same temperature, the volume contraction of the mixtures with water, we see that it is very large for the monatomic alcohols, but decreases with increase in the number of hydroxy-groups. The contraction-maximum at 0° is, for instance:

For ethyl alcohol + water .....	4.00 per cent.
„ glycol „ „ .....	1.55 „
„ glycerol „ „ .....	1.38 „

With sucrose solutions an important contraction (more than 3 per cent.) occurs at a concentration of 70 per cent.; according to the curve (No. III), a more concentrated solution would give a higher contraction. But experiment fails, because water and sucrose are not miscible in all proportions at the ordinary temperature.

As a general rule, the contraction-maximum occurs at a higher concentration as the molecular weight of the substance increases; so that it is quite natural that this maximum is not yet reached at the concentration of 70 per cent. of sugar. By transforming the weight-percentage into molecular-percentage, this maximum would, of course, be displaced to the left; but by doing so, we would seem to accept as true, a priori, the theory that admits the existence of combinations in molecular proportions for determined concentrations; I have (*J. Chim. phys.*, 1911, 9, 57) discussed the reasons against thinking that there is up to the present any evidence of the existence of such combinations.

The change of association that occurs on mixing two liquids is

generally a maximum when the liquids are in nearly the same proportions or in simple molecular relations; it is natural that the volume-change—whatever the reasons of this change may be—should be more pronounced in concentrated than in dilute solutions; but that is not a sufficient reason for assuming the existence of chemical combinations in the solution.

These investigations should be completed by the examination of other substances of the sugar class, and of their solutions in water; the highly associated properties of these compounds promise interesting results.

I desire to express my best thanks to the Committee of Managers for permission to work in the Research Laboratory of the Royal Institution of Great Britain.

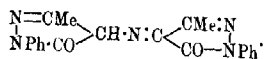
DAVY-FARADAY RESEARCH LABORATORY,  
LONDON.

# CLXX.—*Triketohydrindene Hydrate. Part V. The Analogues of Uramil and Purpuric Acid.*

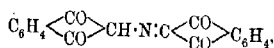
By SIEGFRIED RUHEMANN.

2-OXIMINO-1:3-DIKETOHYDRINDENE,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C:NOH$ , which may be regarded as the violuric acid of the hydrindene group, on treatment with fuming hydriodic acid, yields hydrindantin instead of diketohydrindamine (this vol., p. 1306). The transformation of the oxime into the amine takes place, however, when stannous chloride is used as reducing agent. The base,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} CH \cdot NH_2$ , which is the analogue of uramil, is very unstable, turning brown and then blue on exposure to moist air. Owing to this property, it was not possible to obtain it in a pure state and to verify its composition by analysis, but it could be characterised by the condensation products which it forms with aromatic aldehydes and triketohydrindene hydrate. With benzaldehyde, it condenses to 1:3-diketobenzylidenehydrindamine,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} CH \cdot N:CH \cdot C_6H_5$ , which is orange; with salicylaldehyde, amisaldehyde, and *p*-dimethylamino-benzaldehyde, it yields substances which are of a deeper colour. These compounds, although stable when dry, are hydrolysed gradually by moist air, but readily on boiling with water or alcohol,

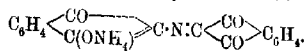
with the production of aldehyde and amine, dark solutions being formed, which, under the influence of the oxygen of the air, turn blue. This behaviour of diketohydrindamine resembles 4-amino-1-phenyl-3-methylpyrazolone,  $C_6H_5 \cdot N \begin{smallmatrix} N=C \cdot CH_3 \\ CO \cdot CH \cdot NH_2 \end{smallmatrix}$ , the uramil of the pyrazolone series. Knorr (*Annalen*, 1887, **238**, 189), who obtained this base by reduction of the corresponding oxime, did not succeed in isolating it; he proved, however, its formation by the analysis of its hydrochloride, and the study of its condensation products with benzaldehyde and 4-keto-1-phenyl-3-methylpyrazolone,  $C_6H_5 \cdot N \begin{smallmatrix} N=C \cdot CH_3 \\ CO \cdot CO \end{smallmatrix}$ . He also indicated the resemblance between the compound which is formed by the action of the diketopyrazole on the amine, and purpuric acid by showing that it yields deep violet solutions with alkalis or ammonia. The constitution of this substance, which was called rubazonic acid, may be represented thus:



This formula corresponds with that of purpuric acid put forward seven years later by Piloty (*Annalen*, 1904, **333**, 68) and by Slimmer and Stieglitz (*Amer. Chem. J.*, 1904, **31**, 661). The condensation product formed by diketohydrindamine with triketohydrindene hydrate, which may be called *diketohydrindylidene-diketohydrindamine*, resembles purpuric and rubazonic acids both in constitution:



and in properties; it differs from those acids mainly in the degree of stability. Although it can be isolated from its ammonium salt on careful treatment with dilute hydrochloric acid, it is very sensitive towards mineral acids and alkalis; purpuric acid, however, does not exist in the free state, whereas rubazonic acid is comparatively stable, being decomposed only on boiling its alkaline solutions. The ammonium salt of the hydrindene analogue of purpuric acid may be represented by the formula:



which corresponds with Slimmer and Stieglitz's formula of murexide. It is formed by the oxidation of diketohydrindamine, and can readily be obtained from hydrindantin under conditions similar to those which Piloty and Finckh (*Annalen*, 1904, **333**, 27) recommend for the preparation of murexide from alloxantin. The

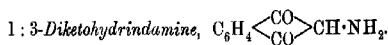
salt is characterised by its property of dissolving in water to yield deep blue solutions. The mode of formation of purpuric acid and its analogues leads to the view that similar substances would be produced by the action of the cyclic di- or tri-ketone with uramil or its analogues. Such a substance can readily be prepared in the form of its potassium salt on treatment of a solution of uramil in potassium hydroxide with triketohydrindene hydrate. This salt of

*diketohydrindylideneuramil*,  $\text{CO} \begin{array}{c} \text{NH} \text{---} \text{CO} \\ \text{NH} \cdot \text{C}(\text{OK}) \end{array} \text{C} \cdot \text{N} : \text{C} \begin{array}{c} \text{CO} \\ \text{CO} \end{array} \text{C}_6\text{H}_4$

dissolves in water to form reddish-violet solutions, which are decolorised immediately on the addition of dilute hydrochloric acid.

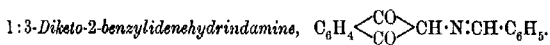
The ease with which hydrindantin is transformed into the analogue of murexide, together with Strecker's results concerning the formation of murexide by the action of amino-acids on alloxan (*Annalen*, 1862, **123**, 363), suggested that the blue colour reaction which triketohydrindene hydrate gives with proteins and their hydrolytic products, is due to the production of the ammonium salt of diketohydrindylidenediketohydrindamine. This view, which is supported by the fact that in both cases the coloration is accompanied by the formation of aldehydes, has been confirmed by the isolation of the salt from the product of the action between alanine and triketohydrindene hydrate. After this substance had been recommended as a reagent for amino-acids (*Trans.*, 1910, **97**, 2025; see also Abderhalden and Schmidt, *Zeitsch. physiol. Chem.*, 1911, **72**, 37), Hurtley and Wootton (this vol., p. 288) expressed the opinion that alloxan will be found of great use in biochemistry, and they based their view on Strecker's results. It appears, however, that alloxan is less valuable for the purpose than triketohydrindene hydrate on account of the inferior sensitiveness of the colour test, especially in the examination of animal fluids (for example, urine), and for the reason that it also gives with ammonia the murexide reaction, which is probably due to the presence of traces of alloxantin in alloxan.

#### EXPERIMENTAL.



On gradually adding finely powdered oximino-1:3-diketohydrindene (5 grams) to stannous chloride (15 grams), dissolved in concentrated hydrochloric acid (30 c.c.), it slowly dissolves with development of heat, and then the whole sets to a semi-solid mass of colourless crystals of a tin double salt of the amine, before the

oxime has entered completely into solution. The mixture is kept at the ordinary temperature for about an hour, the solid collected, washed with a little fuming hydrochloric acid, and dried in a vacuum desiccator over sulphuric acid and soda-lime. It is not advisable to attempt to complete the reduction of the oxime by digesting the mixture on the water-bath, because a partial transformation of the amine into hydrindantin occurs. The dry product is readily soluble in water with the exception of a small quantity of unaltered oxime which is removed by filtration. In order to isolate diketohydrindamine, the yellow solution of the double salt is freed from tin by hydrogen sulphide, and the filtrate from the metallic sulphide, which rapidly turns red, neutralised with ammonium carbonate, when yellow, glistening crystals separate. These are collected, washed with aqueous hydrogen sulphide, and dried in a vacuum desiccator. These operations must be carried out as rapidly as possible, because the amine is extremely sensitive to the oxygen of the air, turning first brown and then blue. Even with the greatest care the product, after drying, was dark coloured. All attempts to purify the substance by crystallisation failed, deep blue solutions being produced on boiling it with water or alcohol. The amine is insoluble in chloroform, and on washing it with boiling chloroform until the filtrate is almost colourless, it is left behind as a yellow, crystalline substance. This, however, does not represent the pure diketohydrindamine as has been ascertained by analysis. The compound reduces ammoniacal silver solutions in the cold, Fehling's solution on slightly warming, and readily reacts with aromatic aldehydes to yield coloured condensation products, which are less stable than 4-benzylideneamino-1-phenyl-3-methyl-pyrazolone.



On mixing the amine with an excess of benzaldehyde, the whole soon sets to a semi-solid mass of orange needles, which are washed, first with alcohol, then with ether, until the filtrate is light yellow, and dried in a vacuum desiccator. The substance melts and decomposes at  $196^\circ$ :

0.2050 gave 0.5800  $CO_2$  and 0.0825  $H_2O$ .  $C=77.16$ ;  $H=4.46$ .

0.2225 „ 11 c.c.  $N_2$  at  $20^\circ$  and 759 mm.  $N=5.64$ .

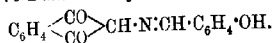
$C_{16}H_{11}O_2N$  requires  $C=77.10$ ;  $H=4.42$ ;  $N=5.62$  per cent.

1:3-Diketo-2-benzylidenhydrindamine is sparingly soluble in ether or cold alcohol; it dissolves in boiling alcohol, but at the same time decomposes into the aldehyde and the amine, which latter is finally oxidised by the oxygen of the air to the analogue of



murexide. Owing to this transformation, the filtrate from the small quantity of orange needles, which on cooling separate from the alcoholic solution, turns deep blue. The substance is hydrolysed also by water, readily on boiling, but slowly at the ordinary temperature, and the odour of benzaldehyde is noticeable on exposing it to the air.

1:3-Diketo-2-salicylidenehydrindamine,

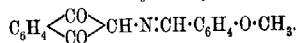


This compound is prepared from salicylaldehyde and diketo-hydrindamine in the same way as the former, and resembles it in its properties. It is orange, and melts and decomposes at 248—249°:

0.2247 gave 10.4 c.c.  $\text{N}_2$  at 19° and 766 mm.  $\text{N} = 5.36$ .

$\text{C}_{16}\text{H}_{11}\text{O}_3\text{N}$  requires  $\text{N} = 5.28$  per cent.

1:3-Diketo-2-anisylidenehydrindamine,

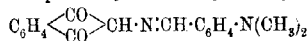


This is sparingly soluble in boiling alcohol, and, at the same time, partly decomposes; from the solution, on cooling, beautiful orange needles separate, which melt and decompose at 215—216°, whereas the dark brown filtrate turns deep blue on contact with the air:

0.1940 gave 0.5193  $\text{CO}_2$  and 0.0825  $\text{H}_2\text{O}$ .  $\text{C} = 73.0$ ;  $\text{H} = 4.72$ .

$\text{C}_{17}\text{H}_{13}\text{O}_3\text{N}$  requires  $\text{C} = 73.12$ ;  $\text{H} = 4.65$  per cent.

1:3-Diketo-2-p-dimethylaminobenzylidenehydrindamine,

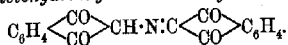


This compound is prepared by mixing an alcoholic solution of *p*-dimethylaminobenzaldehyde with diketo-hydrindamine; after a short time the whole sets to a mass of dark red needles, which are sparingly soluble in boiling alcohol, readily so in hot glacial acetic acid, and crystallise from these solvents in raspberry-coloured needles, melting and decomposing at 239°. The substance is more stable than those described above:

0.1605 gave 13.6 c.c.  $\text{N}_2$  at 20° and 760 mm.  $\text{N} = 9.69$ .

$\text{C}_{18}\text{H}_{16}\text{O}_2\text{N}_2$  requires  $\text{N} = 9.59$  per cent.

*Diketohydrindylidenediketohydrindamine,*



The ammonium salt of this substance, which is the analogue of murexide, is formed by the oxidation of diketohydrindamine or by the action of ammonium carbonate on hydrindantin. It is readily prepared according to the second method by following Piloty and Finckh's directions (*loc. cit.*) for the production of murexide. For this purpose a solution of ammonium acetate (13 grams) in water (50 c.c.) is neutralised with ammonia and mixed with a solution (5 c.c.) of ammonia (10 per cent.), which has been previously saturated with carbon dioxide; to the hot mixture of the ammonium salts, hydrindantin (2.5 grams), suspended in boiling water (250 c.c.), is gradually added with constant stirring, when a brown solid is produced. After about half an hour this is collected, and boiled with water. The dark blue filtrate from which, on cooling, only a small quantity of crystals with metallic lustre separates, is poured into a strong solution of ammonium chloride, when the organic ammonium salt is precipitated. It is washed with water until the filtrate is deep blue, and dried, first in a vacuum desiccator and then in the water-oven:

0.2020 gave 0.5010  $\text{CO}_2$  and 0.0690  $\text{H}_2\text{O}$ .  $\text{C}=67.64$ ;  $\text{H}=3.79$ .

0.2665 „ 20.4 c.c.  $\text{N}_2$  at  $18^\circ$  and 759 mm.  $\text{N}=8.82$ .

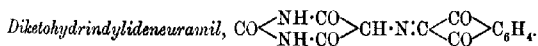
$\text{C}_{18}\text{H}_{12}\text{O}_4\text{N}_2$  requires  $\text{C}=67.50$ ;  $\text{H}=3.75$ ;  $\text{N}=8.75$  per cent.

On adding dilute hydrochloric acid to the cold blue solution of this salt, *diketohydrindylidenediketohydrindamine* is precipitated as a red powder with superficial metallic lustre. This must be collected at once, washed with water, and dried in a vacuum desiccator, because it is unstable in the presence of mineral acids, and gradually dissolves to yield a yellow solution:

0.2410 gave 10.2 c.c.  $\text{N}_2$  at  $21^\circ$  and 770 mm.  $\text{N}=4.88$ .

$\text{C}_{18}\text{H}_8\text{O}_4\text{N}$  requires  $\text{N}=4.62$  per cent.

This analogue of purpuric acid is readily decomposed by potassium hydroxide, as it is by mineral acids; it dissolves in dilute ammonia to form a blue solution of the ammonium salt. This reaction is so sensitive that it is possible by means of this substance to detect the traces of ammonia present in the distilled water of the laboratory.



The potassium salt of this compound is prepared on proceeding as follows. Uramil (0.8 gram) is added to dilute potassium

hydroxide (containing 0.32 gram KHO) after having displaced the air by hydrogen. The solution which is gradually produced on warming, is poured into a solution of triketohydrindene hydrate (1 gram in 10 c.c.). The mixture turns reddish-violet, and in a short time clusters of small, brown needles separate. These are washed with water, and dried in a vacuum desiccator:

0.2570 gave 0.0683  $K_2SO_4$ .  $K=11.91$ .

0.2425 „ 27 c.c.  $N_2$  at  $21^\circ$  and 773 mm.  $N=12.89$ .

$C_{13}H_6O_5N_2K$  requires  $K=12.07$ ;  $N=13.0$  per cent.

The salt on ignition frothes considerably; it is therefore necessary to heat gradually in the determination of the metal. The potassium compound dissolves in water to yield a deep reddish-violet solution, which, on adding dilute hydrochloric acid, is decolorised immediately with the separation of uramil.

#### *Action of Triketohydrindene Hydrate on Amino-acids.*

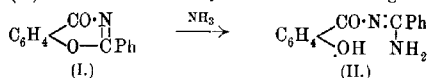
As mentioned before (this vol., p. 793), the blue coloration which the triketone yields with amino-acids is accompanied by the formation of aldehydes, except in the case of glycine, which, on warming its aqueous solution with the reagent, does not yield formaldehyde. This fact corresponds with Strecker's observation (*loc. cit.*; see also Hurlley and Wootton, this vol., p. 288) of the behaviour of alloxan towards glycine. With regard to the other products which are formed in the reaction, it has so far been ascertained that the ammonium salt of diketohydrindylidenediketohydrindamine is produced, and that the colour test is based on the formation of this salt. This fact was established by examining the action of alanine on triketohydrindene hydrate. On mixing warm concentrated aqueous solutions of equal weights of the reagents, a deep blue solution is produced; at the same time acetaldehyde and carbon dioxide are formed, and a dark bluish-brown solid separates. After about half an hour, this is collected, and washed with a little water; it dissolves partly in boiling water, and the blue filtrate, when mixed with ammonium chloride, yields a reddish-brown precipitate. This was proved to be the analogue of murexide by analysis and by the transformation into the corresponding acid. The part which is insoluble in water has not yet been examined.

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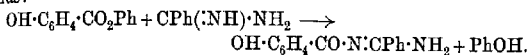
CLXXI.—*The Action of Ammonia and Amines on 2-Phenyl-1:3-benzoxazine-4-one.*

By ARTHUR WALSH TITHERLEY and ERNEST CHISLETT HUGHES.

IT has already been shown by one of the authors (Trans., 1910, 97, 209) that 2-phenyl-1:3-benzoxazine-4-one (I) reacts with aniline readily with ring rupture, forming a yellow compound, salicyl-phenylbenzamidine. The addition of other amines and of ammonia has since been studied closely, and the observations are embodied in the present paper. It has been found that addition takes place with great readiness in all cases, and with ammonia, salicylbenzamidine (II) is formed, which crystallises in fine orange needles:



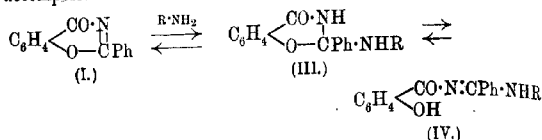
The constitution of the orange compound (II) has been confirmed by its independent synthesis from phenyl salicylate and benzamidine, thus:



In this synthesis a compound,  $\text{C}_{21}\text{H}_{15}\text{ON}_3$ , which crystallises in pale yellow needles, is also formed by a secondary reaction. The constitution of this compound, which has previously been obtained by Pinner (*Ber.*, 1890, 23, 2934, 3824) from ethyl salicylate and benzamidine, is discussed on p. 1499. The authors show that it is formed by the further action of benzamidine on salicylbenzamidine, which was not isolated by Pinner.

2-Phenyl-1:3-benzoxazine-4-one reacts with primary amines in a similar way to ammonia, yielding amidines which are yellow, and have a similar constitution. These amidine derivatives show varying degrees of stability, and while the simple amidine (II) is perfectly stable at  $100^\circ$ , the substituted amidines,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{N} : \text{CPh} \cdot \text{NHR}$ , at  $90$ – $100^\circ$  lose the primary amine  $\text{R} \cdot \text{NH}_2$  more or less readily, with production of the unsaturated cyclic compound (I). This has already been noted in the case of salicylphenylbenzamidine (*loc. cit.*), which readily dissociates at  $100^\circ$ . The methyl and ethyl derivatives (IV) obtained by the addition of methylamine or ethylamine to the cyclic compound (I) are much more thermostable than the phenyl derivative, but on long-continued heating in an open vessel at  $100^\circ$  they lose methylamine and ethylamine respectively, yielding 2-phenyl-1:3-benzoxazine-4-one (I). There can be little doubt that the unstable and hypothetical cyclic compound

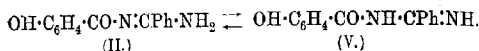
(III) is intermediate, both in the synthetic formation and reversible decomposition in each case:



and a similar mechanism holds in the case of the addition of ammonia, this view being supported by several considerations.

The open-chain amidine derivatives thus exhibit metoxazone tautomerism analogous to that observed among the acyl-salicyl-

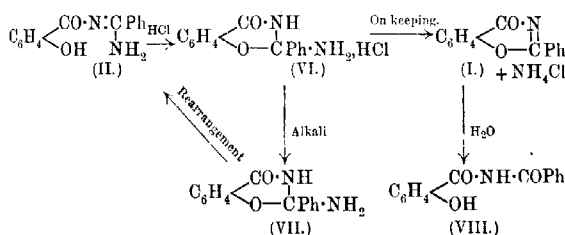
amides, in which the cyclic hydroxy-form,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO}\cdot\text{NH} \\ | \\ \text{O}-\text{CPh}\cdot\text{OH} \end{array}$  is too unstable to exist in a free condition. They also exhibit ename-ketimine (amidine) tautomerism in the open-chain form, and in the case of salicylbenzamidine the tautomeric forms are:



Owing to the bright yellow colour of salicylbenzamidine and its derivatives, and the interest attaching to their true constitution, a close study of their relations has been made, the outcome of which is to make it probable that the ename type of formula (II and IV) is the correct one for the pure solid substances. Their properties, however, including their peculiar behaviour with acids and alkali referred to below, make it impossible to assign the yellow colour to any single type of structure, and these properties seem to be consistent only with the supposition that the open-chain forms are verging on ring-formation, and that the colour is due to some oscillatory play of residual affinities between the hydroxylic and the amidine groupings. Their behaviour with acids may be best illustrated by considering the case of salicylbenzamidine (II). The orange needles, which show both phenolic and basic properties, are insoluble in ammonia, but dissolve in sodium hydroxide to a nearly colourless solution, from which by neutralisation with acids a pale yellow, apparently amorphous precipitate is produced; if rapidly treated with ammonia, this dissolves to a pale yellow solution. From the latter, orange needles of the original substance rapidly separate on keeping. The unstable acid form, soluble in ammonia, may possibly be the imino-compound (V), but it is not possible to isolate it owing to the rapidity with which it is transformed into the orange needles (II).

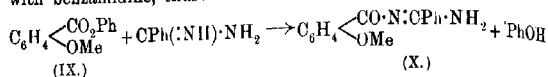
When the solution of the orange needles in alkali is treated with

excess of dilute hydrochloric acid, the yellow precipitate dissolves to a colourless solution, which in a short time deposits a mass of fine colourless needles, consisting of a hydrochloride sparingly soluble in hydrochloric acid. On careful treatment with alkali, the orange-coloured base may be recovered unchanged. The same colourless hydrochloride is obtained by the action of concentrated hydrochloric acid on a solution of the orange compound in acetone. The colour immediately disappears, and a mass of colourless, transparent crystals is deposited. The hydrochloride, freed from acid, on treatment with water, undergoes partial dissociation, giving the solid orange-yellow compound and a pale yellow solution, which on keeping soon becomes turbid, and deposits eventually a pale yellow jelly consisting of *N*-benzoylsalicylamide (white) in a nearly pure form. If water containing a trace of hydrochloric acid instead of pure water is used, the hydrochloride dissolves to a colourless solution, which soon deposits a perfectly white precipitate (microscopic needles) of *N*-benzoylsalicylamide, and the same substance is similarly obtained by the direct treatment of the free base, salicylbenzamidine in aqueous alcohol, with dilute hydrochloric acid. The decomposition is, under ordinary conditions, nearly complete in an hour. The colourless, unstable hydrochloride, for reasons advanced below, is believed to be the cyclic compound (VI), a salt of the cyclic amino-compound (VII), which, however, cannot exist in the free state, but immediately undergoes rearrangement into the orange compound (II). On this view the cyclic hydrochloride in faintly acid aqueous solution suffers gradual loss of ammonia as ammonium chloride, yielding 2-phenyl-1:3-benzoxazine-4-one (I), which, being extremely sensitive to hydrogen ions, immediately suffers hydrolytic fission, as previously shown by one of the authors (Trans., 1910, 97, 209), yielding *N*-benzoylsalicylamide (VIII):

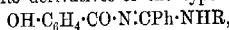


The alternative view that the colourless hydrochloride is a salt of the open-chain base (II) is discountenanced by a consideration of the properties of *o*-methoxybenzoylbenzamidine (X), in which the mobile phenolic hydrogen atom is replaced. This compound was

synthesised from phenyl *o*-methoxybenzoate (IX) by condensation with benzamidine, thus:

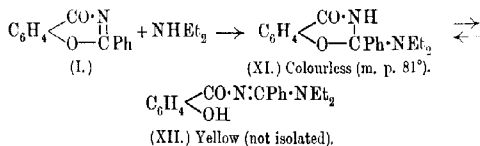


The compound (X) is a quite colourless base, and its hydrochloride is practically unaffected in presence of aqueous hydrochloric acid in the cold. On heating, however, it is slowly converted into *N*-benzoyl-*o*-methoxybenzamide, identical with the compound obtained by McConnan and Titherley (Trans., 1906, **89**, 1332). This relatively difficult hydrolysis by hot acids is the normal decomposition of amidines, and is precisely similar to that which can be effected under similar conditions with benzoylbenzamidine,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{N}\cdot\text{CPh}\cdot\text{NH}_2$ , which yields dibenzamide. The easy hydrolysis of salicylbenzamidine in the cold, and the still more rapid acid hydrolysis of its derivatives of the type



which is complete in the cold in the course of a few minutes, stands out as a different type of reaction from ordinary amidine hydrolysis.

In order to throw further light on the constitution of salicylbenzamidine and its derivatives, the behaviour of 2-phenyl-1:3-benzoxazine-4-one with secondary amines was studied, and for this purpose dimethylamine, diethylamine, and diphenylamine were chosen. Considerable difficulty was experienced, inasmuch as although addition takes place at once in the cold in presence of solvents, mixtures of labile isomeric forms result, which on evaporating give yellow, difficultly crystallisable syrups. In the addition of dimethylamine, separation could not be effected, but with diethylamine a definite crystalline solid was obtained in colourless crystals. This compound from its properties must be 2-diethylamino-2-phenyl-dihydro-1:3-benzoxazine-4-one (XI), and represents the simple additive compound of the unsaturated cycloid (I). It is, however, extremely labile, and slowly turns yellow, even in the solid condition. In solvents, it gives a pale yellow solution, which shows the properties of an equilibrium mixture of the cyclic form (XI) and open-chain, yellow form, salicyldiethylbenzamidine (XII), which, however, could not be isolated in a pure condition:

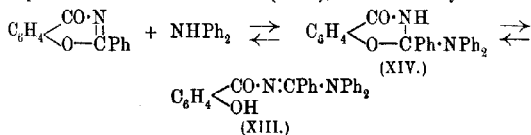


The colourless compound and yellow mixture dissolve at once in

dilute hydrochloric acid, forming a clear, colourless solution of the cyclic hydrochloride, which decomposes with great rapidity, in a similar manner to salicylbenzamidinium. Diethylamine is eliminated, and a white precipitate of *N*-benzoylsalicylamide is produced. The extreme case of this change, which is complete in the course of 5–6 seconds in the cold, confirms the supposition already expressed that in salicylbenzamidinium (II) and all these derivatives the decomposition by acids is not simple amidine hydrolysis, and that acids produce salts of the (colourless) cyclic isomeric forms, which then more or less readily lose ammonia or amines, yielding the unsaturated cycloid (I); the latter, under the influence of acids, combines with water as it is formed, and by ring fission yields *N*-benzoylsalicylamide.

From these considerations it follows that in the majority of cases the stable existent form of these compounds in the free condition is the open-chain amidine form (as in II), which is yellow, whilst the hydrochlorides, which are colourless and more or less rapidly decomposed by water, possess the cyclic constitution, and are derivatives of dihydro-1:3-benzoxazine-4-one (as in VI). The only case observed where the stable form in the free condition possesses this cyclic structure is the diethylamino-derivative, which, however, rapidly comes into equilibrium with the yellow, open-chain amidine form in solution.

The addition of diphenylamine to 2-phenyl-1:3-benzoxazine-4-one (I) gave interesting results. In benzene solution the two combine, giving a deep yellow solution, which yields a syrupy mixture on evaporation. Difficulty was experienced owing to easy reversible dissociability of the additive compound into its constituents. When a hot solution of the unsaturated cyclic compound (I) in light petroleum was treated with an equivalent amount of diphenylamine, a colourless solution resulted, which became pale yellow on cooling. By keeping warm and adding an excess of diphenylamine (which is very soluble in light petroleum), the colour intensified as the increased mass of the diphenylamine increased the amount of the additive compound, until finally it separated out on cooling slightly as a mass of beautiful yellow needles. The constitution of this diphenylamine derivative presents some difficulty. Although its yellow colour, having regard to the above considerations, suggests the open-chain amidine structure (XIII), its insolubility in sodium

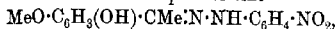






compound (XV), but it is difficult to reconcile with its easy production from salicylphenylbenzamidine (II), which has no tendency to lose ammonia. Moreover, the compound is, like cyaphenine (triphenylcyanidine), devoid of basic properties such as should be associated with Pinner's formula. Taking all the facts into account, the compound must be regarded as *o*-hydroxycyaphenine, and the suppression of ordinary phenolic properties must be attributed to the steric influences already referred to. That the phenolic properties are not entirely suppressed has been shown by the authors in the fact that, although the compound gives no ferric chloride reaction and is not affected by aqueous sodium hydroxide, it yields with sodium ethoxide in alcohol a bright yellow sodium derivative, which is decomposed by excess of water with production of the unchanged compound.

A similar case of disappearance of phenolic properties has been lately observed by Torrey and Adams (*Ber.*, 1910, **43**, 3227) in certain hydrazone derivatives of pæonol like



which is not affected by alkali. The position of the hydroxyl group is similar in these derivatives to those of the authors.

#### EXPERIMENTAL.

##### *Salicylbenzamidine*, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} : \text{N} \cdot \text{CPh} \cdot \text{NH}_2$ .

(1) *Preparation from 2-Phenyl-1:3-benzoxazine-4-one*.—Twenty grams of 2-phenyl-1:3-benzoxazine-4-one dissolved in 200 c.c. alcohol were saturated with gaseous ammonia, and the bright yellow solution was allowed to evaporate. Salicylbenzamidine (20 grams) separated as a mass of practically pure, transparent, orange-yellow needles. By recrystallisation from a mixture of benzene and light petroleum (1:3), the compound was obtained in silky, orange needles, melting at 136°.

An alternative method of preparation consisted in treating the alcoholic solution of 2-phenyl-1:3-benzoxazine-4-one with concentrated aqueous ammonia, when, after half an hour, salicylbenzamidine separates as a mass of orange needles in nearly quantitative yield:

0.1669 gave 17.3 c.c.  $\text{N}_2$  at 23° and 743 mm.  $\text{N} = 11.42$ .

$\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_2$  requires  $\text{N} = 11.66$  per cent.

(2) *Preparation from Phenyl Salicylate*.—Two grams of phenyl salicylate were mixed with 1 gram of benzamidine, freshly prepared from its hydrochloride, when an immediate reaction took place with evolution of heat. A yellow colour developed, and a mass of nearly white crystals, probably the phenyl salicylate salt of benzamidine,

were deposited. About 20 c.c. of alcohol were now added, and the mixture heated to the boiling point. A rapid reaction took place with formation of a clear, bright yellow solution, from which in a few moments a mass of nearly colourless, short, silky needles separated (0.15 gram). These melted at  $248^{\circ}$ , and consisted of *o*-hydroxytriphenylcyanidine (p. 1498). (Found, N=12.69. Calc., N=12.90 per cent.)

The alcoholic filtrate on careful dilution with water gave salicylbenzamidine as a mass of orange-yellow needles (0.8 gram), melting, after recrystallisation from a mixture of benzene and light petroleum, at  $136-137^{\circ}$ :

0.2889 gave 28.3 c.c.  $N_2$  at  $17^{\circ}$  and 764 mm. N=11.43.

$C_{14}H_{12}O_2N_2$  requires N=11.66 per cent.

*Salicylbenzamidine* is readily soluble in alcohol, acetone, or chloroform, moderately so in ether or benzene, and practically insoluble in light petroleum. Its solution in acetone gives an intense purple-red colour with alcoholic ferric chloride. It is immediately soluble in dilute sodium hydroxide to a very pale yellow solution, which with dilute hydrochloric acid gives a yellow precipitate, which at once dissolves in excess of acid. The resulting colourless solution, after one minute, deposits a thick mass of fine white needles, consisting of a hydrochloride insoluble in hydrochloric acid. The hydrochloride on keeping soon changes to *N*-benzoylsalicylamide. Even if it is rapidly collected this decomposition cannot be avoided, and on washing the precipitate it becomes pale yellow, owing to partial dissociation. The pure *hydrochloride* was obtained by treating a solution of 1 gram of salicylbenzamidine in 15 c.c. of acetone with 1 c.c. of concentrated hydrochloric acid. It separated after a short time as a mass of small, colourless needles (1.25 grams), which were washed with acetone and dried in a vacuum, in which, however, slight dissociation occurred, and a slightly yellow colour developed. It was analysed by decomposition with water containing a small quantity of nitric acid. The *N*-benzoylsalicylamide formed was weighed, and the hydrochloric acid determined by titration:

0.2078 gave 0.1650 *N*-benzoylsalicylamide (theory 0.1810) and required 7.1 c.c.  $N/10\text{-AgNO}_3$ . Cl=12.13.

$C_{14}H_{12}O_2N_2.HCl$  requires Cl=12.8 per cent.

The hydrochloride on heating to  $120^{\circ}$  partly melted, and lost ammonium chloride, giving 2-phenyl-1:3-benzoxazine-4-one, which was isolated by extraction with benzene, washing the benzene solution with alkali, and evaporating. After recrystallisation from light petroleum, it melted at  $106^{\circ}$ , and gave the characteristic reaction with hydrochloric acid (Trans., 1910, **97**, 207).

The hydrochloride dissolves fairly readily in alcohol with slight dissociation and a faint yellow colour. This solution gives a port-wine tint with alcoholic ferric chloride, but if previously treated with very dilute alcoholic hydrogen chloride until just colourless the solution gives no ferric chloride coloration.

The hydrochloride is partly dissociated by water, forming a pale yellow solution, and generally leaving a little free base insoluble as a yellow solid, but a colourless solution results if a small quantity of free hydrochloric acid is added. The pale yellow aqueous solution on being kept for a few minutes deposits pale yellow needles (m. p.  $132^{\circ}$ ) of salicylbenzamidine, and later a sulphur-yellow precipitate, consisting of a mixture of this and *N*-benzoylsalicylamide. The acidified colourless solution on keeping deposits continually a white precipitate of pure *N*-benzoylsalicylamide (m. p.  $208^{\circ}$ ). The decomposition is nearly complete in an hour at the ordinary temperature, as shown in the curve on p. 1508; at higher temperatures it is practically instantaneous.

*Salicylmethylbenzamidine*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{N}\cdot\text{CPh}\cdot\text{NHMe}$ .

One gram of 2-phenyl-1:3-benzoxazine-4-one in saturated alcoholic solution was treated with 0.45 gram of a 33 per cent. aqueous solution of methylamine. A yellow colour was immediately produced, and after some time salicylmethylbenzamidine separated in large, yellow, hexagonal plates, leaving a yellow syrup. After washing with dilute alcohol and recrystallising from light petroleum, it was obtained in bundles of yellow needles, melting at  $95^{\circ}$ :

0.6332, by Kjeldahl's method, required 50.0 c.c. *N*/10-HCl.  
N = 11.06.

$\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_2$  requires N = 11.03 per cent.

*Salicylmethylbenzamidine* is fairly soluble in the cold in alcohol or ether, and readily so in acetone or benzene. It is easily soluble in all hot solvents. It gives a strong red coloration with ferric chloride. On heating at  $90$ – $100^{\circ}$ , it gradually loses methylamine, and leaves 2-phenyl-1:3-benzoxazine-4-one, the yield of which on small quantities is nearly theoretical in six days (0.1270 gave 0.1130; theory requires 0.1115). *Salicylmethylbenzamidine* dissolves in sodium hydroxide to a very pale yellow solution, and in dilute hydrochloric acid to a colourless solution, from which *N*-benzoylsalicylamide is rapidly deposited, the decomposition being practically complete at  $15^{\circ}$  in about fifteen minutes.

*Salicylethylbenzamidine*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{N}:\text{CPh}\cdot\text{NHEt}$ .

A saturated alcoholic solution of 3 grams of 2-phenyl-1:3-benzoxazine-4-one was treated with 3 grams of 33 per cent. aqueous ethylamine. A yellow colour was produced immediately, and in a short time yellow needles of salicylethylbenzamidine formed, which were collected after three hours. The yield was 2 grams, and the compound, after recrystallising from light petroleum, melted at 118—119°:

0.4824, by Kjeldahl's method, required 35.5 c.c.  $N/10\text{-HCl}$ .  $N=10.30$ .

$\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_2$  requires  $N=10.45$  per cent.

*Salicylethylbenzamidene* is very sparingly soluble in cold ether or light petroleum, readily so in cold acetone or benzene, and moderately so in cold alcohol. When heated at 90—100° it slowly loses ethylamine, leaving 2-phenyl-1:3-benzoxazine-4-one (m. p. 106°), the decomposition being complete in six days. (0.1340 gave 0.1120, theory requires 0.1115.) Salicylethylbenzamidene gives a deep red coloration with ferric chloride; it dissolves in sodium hydroxide to a very pale yellow solution, and in dilute hydrochloric acid to a colourless solution, from which *N*-benzoylsalicylamide is rapidly deposited, the decomposition being practically complete at 15° in five minutes.

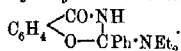
*Action of Dimethylamine on 2-Phenyl-1:3-benzoxazine-4-one.*

The interaction between these substances was tried under a variety of conditions, using ether, alcohol, benzene, and light petroleum as solvents, and in each case yellow solutions were obtained, which on evaporation left viscid, yellow syrups. The latter evidently consisted of a mixture of salicyldimethylbenzamidine and 2-dimethylamino-2-phenyldihydro-1:3-benzoxazine-4-one, and on keeping in a vacuum for several weeks partly crystallised, but owing to the tendency which these two compounds have to suffer rearrangement, forming an equilibrium mixture, it was found impossible to effect a proper separation. The crystals, which were obtained only in very small quantity, melted at temperatures between 90° and 106°. A determination of nitrogen in the syrupy mixture was made:

0.2244, by Kjeldahl's method, required 16.8 c.c.  $N/10\text{-HCl}$ .  $N=10.48$ .

$\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_2$  requires  $N=10.45$  per cent.

The mixture gave a deep reddish-violet colour with ferric chloride, and was rapidly decomposed by dilute hydrochloric acid, yielding dimethylamine and *N*-benzoylsalicylamide.

*Action of Diethylamine on 2-Phenyl-1:3-benzoxazine-4-one.**2-Diethylamino-2-phenyldihydro-1:3-benzoxazine-4-one,*

Similar difficulties were encountered to those mentioned in the case of dimethylamine, but after several trials one of the two products formed (the cyclic diethyl derivative) was definitely isolated as follows: Five grams of 2-phenyl-1:3-benzoxazine-4-one in 50 c.c. of pure benzene were treated with a solution of 1.5 grams of diethylamine in benzene. A yellow colour rapidly developed, and on vaporation at 15° a yellow syrup was left, which in a few days set to a crystalline mass. The solid consisted essentially of the cyclic base, and after draining weighed 5.5 grams. By careful treatment with cold 5 per cent. aqueous sodium hydroxide, the isomeric yellow salicyldiethylbenzamidine present was removed, leaving a white solid (5 grams). Attempts to obtain salicyldiethylbenzamidine from the alkaline filtrate by cautious treatment with citric acid or carbon dioxide gave only *N*-benzoylsalicylamide, diethylamine being eliminated. The solid remaining after treatment with alkali was recrystallised by dissolving in alcohol at 6°, and cautiously adding water; on keeping, pure 2-diethylamino-phenyldihydro-1:3-benzoxazine-4-one separated in colourless needles, melting at 81°, and weighing 3 grams:

0.4124, by Kjeldahl's method, required 27.0 c.c. *N*/10-HCl.  
N=9.17.

$\text{C}_{18}\text{H}_{20}\text{O}_2\text{N}_2$  requires N=9.46 per cent.

The cyclic base undergoes partial rearrangement to the yellow pen-chain isomeride, even in the solid condition, and the change can be traced in the yellow colour which the colourless crystals acquire on keeping a few hours. The tautomeric change appears to be practically instantaneous in solution. The compound dissolves easily in cold benzene, acetone, or chloroform to pale yellow solutions, which leave a syrupy mixture of the two isomerides on spontaneous evaporation. In carbon tetrachloride and ethyl acetate, in which the compound is readily soluble, and in alcohol, in which it is moderately soluble, the yellow colour is only very slight, and the equilibrium between the colourless ring and yellow pen-chain isomerides is clearly dependent on the nature of the solvent. The solutions in alcohol and acetone give a reddish-violet colour with ferric chloride. The cyclic base, like salicylmethylbenzamidine and salicylethylbenzamidine, readily dissociates on heating above 90°. Diethylamine is lost, and after heating for fifteen hours the liquid sets to a crystalline mass of 2-phenyl-1:3-benz-

oxazine-4-one, melting at 103°. The behaviour of the compound with hydrochloric acid was studied in order to throw light on the action of hydrochloric acid on salicylbenzamidine (p. 1500). The cyclic base dissolves readily in excess of cold dilute hydrochloric acid to a colourless solution, which, if the solution is not too dilute, in a few seconds deposits a white, microcrystalline precipitate of the hydrochloride. The latter on warming with aqueous ammonia dissolves to a bright yellow solution, which on cooling deposits a mass of needles of salicylbenzamidine, melting at 135°. 2-Phenyl-1:3-benzoxazine-4-one is undoubtedly first produced, and then combines with ammonia, and the same mechanism explains the ready decomposition of the hydrochloride with water. When the cyclic base in a finely divided state is suspended in sufficient water (to prevent the hydrochloride being precipitated), on adding dilute hydrochloric acid a clear solution is formed, but hydrolysis rapidly takes place, and an abundant precipitate of *N*-benzoylsalicylamide (m. p. 200°) begins to be deposited in about five seconds. By collecting at short intervals it was found that the decomposition (with formation of diethylamine) was practically complete in three minutes. The hydrochloride of the cyclic base is therefore very much more rapidly hydrolysed than that of 2-amino-2-phenyl-dihydro-1:3-benzoxazine-4-one (p. 1501).

The pure hydrochloride was obtained by treating a solution of 2 grams of the cyclic base in benzene solution with dry hydrogen chloride:

0.0740 required 2.15 c.c. *N*/10-AgNO<sub>3</sub>. Cl=10.31.

C<sub>18</sub>H<sub>21</sub>O<sub>2</sub>N<sub>2</sub>Cl requires Cl=10.38 per cent.

The hydrochloride rapidly decomposes in moist air, and after twenty-four hours contained only 5.61 per cent. of chlorine. At the end of three weeks the remaining white solid consisted almost entirely of *N*-benzoylsalicylamide.

*Action of Diphenylamine on 2-Phenyl-1:3-benzoxazine-4-one.*

*Salicyldiphenylbenzamidine*, OH·C<sub>6</sub>H<sub>4</sub>·CO·N:CPh·NPh<sub>2</sub>. — A solution of 2.3 grams of 2-phenyl-1:3-benzoxazine-4-one in dry benzene was treated with a benzene solution of 1.7 grams of diphenylamine. A bright yellow colour was produced at once, and on allowing to evaporate, a syrup remained, which slowly crystallised. After draining and recrystallising from benzene, *salicyldiphenylbenzamidine* was obtained as a bright yellow, crystalline powder, melting at 92°:

0.6012, by Kjeldahl's method, required 30.1 c.c. *N*/10-HCl.  
N=7.01.

C<sub>26</sub>H<sub>20</sub>O<sub>2</sub>N<sub>2</sub> requires N=6.98 per cent.

The compound gives no reaction with ferric chloride, and is insoluble in sodium hydroxide.

It is sparingly soluble in cold light petroleum, moderately so in cold alcohol or ether, and readily so in cold acetone or benzene, giving yellow solutions in each case. The yellow colour is not lost in hot alcohol, but it disappears in excess of hot benzene or light petroleum, and reappears on cooling, owing to the ready dissociation of the compound into 2-phenyl-1:3-benzoxazine-4-one and diphenylamine. The former can, in fact, be isolated from the hot light petroleum solution, if not too dilute, by cooling. An alternative method of preparation consisted in adding an excess of diphenylamine to a hot solution of 2-phenyl-1:3-benzoxazine-4-one in light petroleum, and allowing to cool, when the compound separated in bright yellow, silky needles melting at  $92^{\circ}$ .

*Action of Piperidine on 2-Phenyl-1:3-benzoxazine-4-one.*

A yellow syrup only could be obtained, consisting apparently of open-chain and cyclic isomerides, which could not be separated. The syrup was easily soluble in benzene and acetone, and was practically insoluble in alkali. With acids, it yielded *N*-benzoylsalicylamide.

*o*-Methoxybenzoylbenzamidine,  $\text{MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{N} : \text{CPh} \cdot \text{NH}_2$ .

The object in synthesising this compound was to compare its properties with those of salicylbenzamidine, and its synthesis was effected from benzamidine and phenyl *o*-methoxybenzoate, which was obtained from *o*-methoxybenzoic acid by a modification of the method described by Seifert (*J. pr. Chem.*, 1844, [ii], **31**, 474). *o*-Methoxybenzoic acid has been obtained by several methods (Cahour, *Annalen*, 1854, **92**, 315; Graebe, *Annalen*, 1866, **139**, 137; Graebe and Ullmann, *Ber.*, 1896, **29**, 825; Bromwell, *Amer. Chem. J.*, 1898, **19**, 577; Weida, *Amer. Chem. J.*, 1898, **19**, 552; Lander, *Trans.*, 1900, **77**, 745), but as on trial these methods gave unsatisfactory yields it was prepared by the authors from salicylamide by methylation and subsequent hydrolysis as follows:

*o*-Methoxybenzamide.—Thirty grams of salicylamide in 200 c.c. alcohol were treated with a solution of 4.6 grams of sodium in 50 grams of alcohol, and then with 40 grams of methyl iodide. After boiling for an hour and a-half and distilling off most of the alcohol, *o*-methoxybenzamide was precipitated with water. It was purified by digesting with sodium hydroxide and recrystallising from hot water (yield 25 grams, m. p.  $128^{\circ}$ ).

*o*-Methoxybenzoic Acid.—Twenty-five grams of *o*-methoxybenz-



amide were boiled with 60 c.c. of 10 per cent. sodium hydroxide for forty-five minutes, when the hydrolysis was complete. On cooling, diluting with water, and acidifying, *o*-methoxybenzoic acid was precipitated, and recrystallised from hot water (yield 18 grams, m. p. 93°).

*Phenyl o-Methoxybenzoate*.—Fifteen grams of *o*-methoxybenzoic acid mixed with 15 grams of freshly distilled phosphoryl chloride were treated at 75° with 9 grams of phenol, and the whole kept at 75° for four hours. The resulting red liquid after cooling was treated with water and shaken with 10 per cent. sodium hydroxide, and the insoluble oil extracted with ether. On evaporation a red oil remained, which solidified on stirring with a little dilute sodium hydroxide. The solid phenyl *o*-methoxybenzoate was purified by recrystallising first from aqueous alcohol and finally from pure alcohol, from which it separated in colourless, six-sided prisms, weighing 17 grams, and melting at 59°.

*Condensation of Phenyl o-Methoxybenzoate and Benzamidine*.—Five grams of phenyl *o*-methoxybenzoate in 10 c.c. of alcohol were treated with 6 grams of benzamidine, and the mixture heated to 50° for ten minutes. On cooling and adding water, *o*-methoxybenzoyl benzamidine (8 grams) was precipitated as a mass of colourless needles, which, after recrystallising from a little alcohol, melted at 128°:

0.2386, by Kjeldahl's method, required 18.7 c.c. *N*/10-HCl.  
 $N = 10.97$ .

$C_{15}H_{14}O_2N_2$  requires  $N = 11.02$  per cent.

*o-Methoxybenzoylbenzamidine* is moderately soluble in cold alcohol, ether, or benzene, and readily so in acetone. It dissolves at once in dilute hydrochloric acid, forming a clear solution, which is only very slowly decomposed at 15°, but at 50° begins after half an hour to deposit *N*-benzoyl-*o*-methoxybenzamide in long needles. (Found:  $N = 5.76$ . Calc.,  $N = 5.50$  per cent.) The stability of the hydrochloride in presence of dilute hydrochloric acid was compared with that of salicylbenzamidine and benzoylbenzamidine,  $NBz:CPH:NH_2$ .

The latter compound, which has been described by Pinner (*Ber.*, 1878, 11, 764; 1889, 22, 1606) and by Beckmann and Sandel (*Annalen*, 1897, 296, 285), was prepared by the authors by the condensation of phenyl benzoate (10 grams) and benzamidine (7.2 grams), which were heated at 50° for three hours. On cooling and adding water, an oil was precipitated, which was treated with dilute hydrochloric acid to separate the benzoylbenzamidine, which dissolved, from unchanged phenyl benzoate (1.5 grams). The acid filtrate on treatment with alkali gave the base as an oil, which

rapidly solidified (7 grams). After recrystallisation from light petroleum it was obtained in fine colourless needles, melting at 98°. In comparing the relative stability of the three amidines towards hydrochloric acid, attempts were made to carry out the measurements under strictly similar conditions, but whilst this is possible as between benzoylbenzamidinium and *o*-methoxybenzoylbenzamidinium, which are only very slowly decomposed, giving dibenzamide and *N*-benzoyl-*o*-methoxybenzamide respectively, in the case of salicylbenzamidinium the hydrolysis is too rapid. Further, owing to the slight solubility in hydrochloric acid of the cyclic hydrochloride resulting from the latter, more water was necessary than can be used in the case of the first two amidines, since the basis of the measurements depended on weighing the resulting secondary amides, which are appreciably soluble in water; the secondary amide derived from salicylbenzamidinium, however (*N*-benzoylsalicylamide), is extremely insoluble in water, excess of which does not therefore vitiate the results. The first experiments give a comparison between benzoylbenzamidinium and *o*-methoxybenzoylbenzamidinium. Two portions of 0.5 gram in each case were dissolved in 10 c.c. of 10 per cent. hydrochloric acid, and the resulting clear solutions allowed to remain (1) at 15°, and (2) at 40°. The crystalline secondary amide produced by hydrolysis was weighed after twenty-four hours in (1), and at intervals in (2), the readings being shown in Fig. 1.

*Benzoylbenzamidinium* (0.5 gram).

(1).	Temp.	Time.	Weight of dibenzamide.	Percentage hydrolysed.
	15°	24 hours	0.13 gram	25.8

*o*-Methoxybenzoylbenzamidinium (0.5 gram).

Temp.	Time.	Weight of <i>N</i> -benzoyl- <i>o</i> -methoxybenzamide	Percentage hydrolysed.
15°	24 hours	0.03 gram	5.9

In the second group of experiments salicylbenzamidinium was treated with the same volume of dilute hydrochloric acid, containing one, two, and three molecular equivalents of hydrogen chloride respectively. 0.2 Gram of the substance was dissolved in (i) 8.4 c.c. of *N*/10-hydrochloric acid and 16.8 c.c. of water; (2) 16.8 c.c. of *N*/10-hydrochloric acid and 8.4 c.c. of water; and (3) in 25.2 c.c. of *N*/10-hydrochloric acid. At higher concentrations than these it is impossible to prevent the insoluble hydrochloride being precipitated. The temperature was kept at 15°, and the insoluble *N*-benzoylsalicylamide which continually separated out, was collected at intervals, dried, and weighed. The results are expressed in Fig. 2.

(2).

FIG. 1.

I. Benzoyl benzamidine (0.5 gram) at 40°.

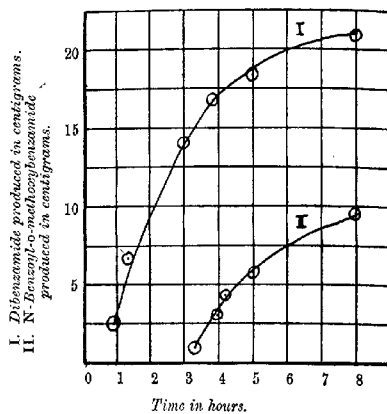
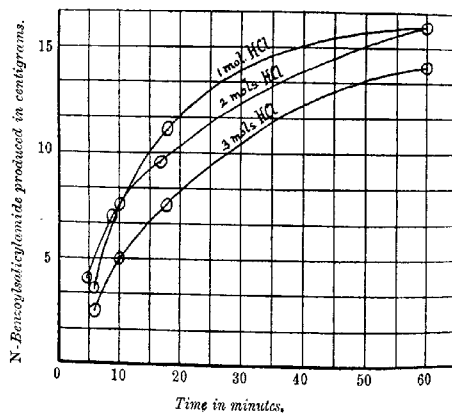
II. *o*-Methoxybenzoylbenzamidine (0.5 gram) at 40°.

FIG. 2.

*Salicylbenzamidine* (0.2 gram) at 15°.

From a comparison of these curves, although the conditions are not the same, it is evident that the velocity of hydrolysis of salicylbenzamidine is vastly greater than that of the other two amidines, even at a higher temperature. It is noteworthy that of the two latter, *o*-methoxybenzoylbenzamidine is hydrolysed much more slowly than benzoylbenzamidine, and this is probably due to steric hindrance. The results in any case are only approximate, since molecular quantities were not taken, and owing to the error due to the slight solubility in water and supersaturation tendency of dibenzamide and *N*-benzoyl-*o*-methoxybenzamide. An unexpected feature in the case of salicylbenzamidine is the slightly inhibitory effect of excess of hydrochloric acid, which appears to increase the stability of the hydrochloride. This effect is probably connected with the fact, previously referred to, that in stronger solutions the hydrochloride is precipitated as a crystalline solid by excess of hydrochloric acid. The reverse effect would be expected if the decomposition were true hydrolysis, and increase in the concentration of the acid catalyst would cause corresponding increase in the velocity of hydrolysis. As it appeared therefore that the mechanism of decomposition was one in which ammonia was eliminated from the cyclic hydrochloride, yielding 2-phenyl-1:3-benzoxazine-4-one as the first product, it appeared to be desirable to examine the velocity of addition of water to this compound (producing *N*-benzoylsalicylamide) under the influence of varying quantities of hydrochloric acid. Alcoholic solutions of 2-phenyl-1:3-benzoxazine-4-one diluted with water to incipient turbidity were treated with the acid, and the resulting precipitate collected at intervals, but it was found that in all cases the velocity was so great that proper measurements could not be made. With one molecular equivalent of dilute alcoholic hydrochloric acid at *N*/40-concentration, the reaction is practically complete in sixty seconds. With 1/45 of the molecular equivalent of acid at *N*/3000-concentration the reaction is complete in eight minutes. As the velocity of decomposition is greater than that of salicylbenzamidine and its derivatives, it would appear that the rate of decomposition of the latter by hydrochloric acid is controlled by the rate at which ammonia or amines are eliminated from their cyclic hydrochlorides.

Condensation of (1) 2-Phenyl-1:3-benzoxazine-4-one, and  
(2) Salicylbenzamidine, with Benzamidine.

*o*-Hydroxytriphenyleyanidine,  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{C}\begin{smallmatrix} \text{N:CPh} \\ \text{N:CPh} \end{smallmatrix}\text{N}$ .—This compound, under another constitutional formula, has already been described by Pinner (*loc. cit.*).

(1) A saturated alcoholic solution of 4.6 grams of 2-phenyl-1,3-benzoxazine-4-one was treated with an alcoholic solution of 2 grams of benzamidine freshly prepared from 2.8 grams of the hydrochloride. An immediate yellow colour was produced, which in the course of a few seconds gave place to a pale yellow, microcrystalline precipitate of pure *o*-hydroxytriphenylcyanidine. After washing with alcohol, it weighed 6.2 grams, and melted at 245°. A further small quantity was obtained from the filtrate on keeping. (Found: N=13.00. Calc., N=12.92 per cent.)

(2) A saturated alcoholic solution of 1 gram of salicylbenzamidine was heated with 0.35 gram of benzamidine for several hours. The cyanidine derivative slowly separated from the hot solution as a pale yellow solid in a practically pure form (0.3 gram). It was identical in all respects with that prepared by method (1) and with the by-product (p. 1500) obtained in the condensation between benzamidine and phenylsalicylate.

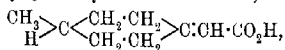
The compound does not show normal phenolic properties. Attempts to methylate it by diazomethane and to acetylate it by acetic anhydride and pyridine failed entirely. On treating with sodium ethoxide in alcohol, however, a bright yellow sodium salt was obtained, which was completely decomposed by water, forming the original compound.

ORGANIC LABORATORY,  
UNIVERSITY OF LIVERPOOL.

## CLXXII.—*Optically Active Derivatives of 1-Methylcyclohexylidene-4-acetic Acid.*

By WILLIAM HENRY PERKIN, jun., and WILLIAM JACKSON POPE.

DURING recent years we have described the preparation (Perkin and Pope, *Trans.*, 1908, **93**, 1075) and resolution into optically active components (Perkin, Pope, and Wallach, *Trans.*, 1909, **95**, 1789) of 1-methylcyclohexylidene-4-acetic acid,

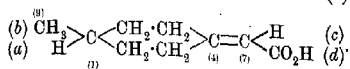


a substance which, although its molecule contains no asymmetric atom, is nevertheless resolvable into components exhibiting optical activity in solution.

We have indicated that the optical activity is due to the enantiomorphous configuration of the molecule as a whole, and that this

kind of enantiomorphism cannot be distinguished by the location of an asymmetric atom in the molecule. The discovery of the new type of optically active substances referred to involves a considerable extension of the whole subject of stereochemistry; it is hence not surprising that our statement that the acid referred to above contains no asymmetric carbon atom in its molecule should have been contested.

The most ample criticism of our results has been published by Everest (*Chem. News*, 1909, **100**, 295), whose attitude is summarised in the following extract from his paper. He observes that "it appears doubtful whether the carbon atom (1) is not asym-



metric, and thus the cause of the optical activity. For beyond the hydrogen atom (a) and the methyl group (b) the configuration of the remainder of the molecule must be considered in order to decide the question, and it is here that I think the authors assume too much when they take it that the configuration of the remainder of the molecule is the same when taken either way, relative to the carbon atom (1); for such is assumed if the carbon atom (1) is said not to be asymmetric."

That this criticism will not withstand examination will be made clear by the following three remarks. (a) An asymmetric atom is never the cause of optical activity; optical activity is apparently invariably, and asymmetry of a carbon atom is in special cases, the result of enantiomorphism of molecular configuration. Optical activity and the presence in the molecule of an asymmetric atom cannot be considered as mutually related in the sense of cause and effect. (b) We have never made the assumption stated in the italicised portion of the above quotation, and have indeed indicated quite clearly (*Trans.*, 1909, **95**, 1792) the erroneous nature of such an assumption. The consideration of a few simple molecular models will show that in any substance of enantiomorphous molecular configuration, the aspect of the arrangement, viewed from any component atom, is always enantiomorphous. (c) If Everest's view that a carbon atom is non-asymmetric only when "the configuration of the remainder of the molecule is the same when taken either way, relative to the carbon atom," is accepted, every atom, carbon, oxygen, or hydrogen, in the molecule of 1-methylcyclohexylidene-4-acetic acid—and indeed of any optically active substance—is asymmetric.

It must thus be granted that our original conclusion stands, and that in 1-methylcyclohexylidene-4-acetic acid we have realised for

the first time the existence of the most general type of enantiomorphism of molecular configuration foreseen by van't Hoff, a type which gives rise to optical activity, but in which no asymmetric atom can be distinguished.

In order to discriminate between this new type of enantiomorphous compound and those substances in which the enantiomorphism of molecular configuration is associated with the presence of an asymmetric carbon, nitrogen, or other atom in the molecule, it is convenient to introduce a special term; we shall refer to such substances as "centrosymmetric." A second example of the centrosymmetric optical activity has been recently described by Mills and Bain (Trans., 1910, 97, 1866) in the oxime of cyclohexanone-4-carboxylic acid,  $\text{CO}_2\text{H} \cdot \text{C} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{C} \cdot \text{N} \cdot \text{OH}$ .

The discovery of the new type of optical activity leads to the enunciation of a stereochemical problem which has never before presented itself, namely, the question as to what will occur when an optically active substance of which the enantiomorphism of molecular configuration is associated with one particular type of asymmetry is converted into a second substance of which the optical activity arises from the exhibition by the molecule of enantiomorphism of a quite different type. With the aid of the optically active 1-methylcyclohexylidene-4-acetic acids, it is possible to study the mode in which the optical activity is affected when the centrosymmetric substance is converted into, or is produced from, one containing an asymmetric carbon atom; the examination of these cases is of considerable interest in connexion with the mechanism of chemical change, and we have therefore investigated a number of such reactions.

#### *Reduction of dl-, d-, and l-1-Methylcyclohexylidene-4-acetic Acids.*

As a preliminary to studying the conversion of the optically active 1-methylcyclohexylidene-4-acetic acids into other potentially optically active substances, it seemed desirable to check the anticipations from theory in connexion with some more simple cases, those, namely, in which the centrosymmetric compounds are converted into others which should be potentially optically inactive. The reduction of 1-methylcyclohexylidene-4-acetic acid to the 1-methylcyclohexyl-4-acetic acid,  $\text{CHMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , would be expected to destroy the enantiomorphism of molecular configuration, and in accordance with this anticipation it is found that the reduction products of the optically active centrosymmetric acids are optically inactive.

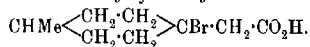
*dl*-1-Methylcyclohexylidene-4-acetic acid is readily and completely

reduced when treated with hydrogen under the conditions described by A. Shika (*Ber.*, 1909, **42**, 1630). Gum arabic (30 c.c. of a 25 per cent. aqueous solution) is mixed with warm water (80 c.c.), 0.5 gram of palladous chloride in aqueous solution added, and, after mixing with a solution of the unsaturated acid (10 grams) in methyl alcohol (100 c.c.), the whole is transferred to a long, narrow cylinder, and a rapid stream of hydrogen passed for two days. The product is distilled in a current of steam, when, after the bulk of the methyl alcohol has been removed, a solid acid passes over with the condensed water. This, when collected and recrystallised from a very little formic acid, is obtained in glistening plates, melting at 71—73°. (Found, C=69.1; H=10.3. Calc., C=69.2; H=10.2 per cent.)

That this acid is 1-methylcyclohexyl-4-acetic acid was proved by mixing it with a specimen of the latter which we had previously obtained synthetically (*Trans.*, 1908, **93**, 1081); the mixture melted at 71—73°. The reduction of 1-methylcyclohexylidene-4-acetic acid under the conditions described proceeds remarkably smoothly and is quite complete; this is shown by the fact that the acid obtained direct from the distillation in steam is stable towards permanganate.

On repeating this preparation with *d*- and *l*-1-methylcyclohexylidene-4-acetic acids, an optically inactive acid, identical with the above saturated acid, is in each case obtained. As was to be anticipated, the conversion of the optically active centrosymmetric acids into a product of which the molecule exhibits none of the characteristics of enantiomorphous configuration, results in the loss of the optical activity.

4-Bromo-1-methylcyclohexyl-4-acetic Acid,



A reaction which resembles the above reduction in that it should convert the centrosymmetric optically active acid into a saturated substance which is potentially optically inactive, is involved in the addition of hydrogen bromide to the 1-methylcyclohexylidene-4-acetic acids. When the unsaturated *dl*-acid is mixed with fuming hydrobromic acid (saturated at 0°) it dissolves, but in a short time an oil, which rapidly crystallises, separates on the surface. The crystalline mass is washed with water, left in contact with porous earthenware until quite dry, and then recrystallised from a little formic acid (*D*=1.22), in which it is very soluble, and from which it separates, usually in plates, but sometimes in hard, brilliant prisms. (Found, Br=34.0. Calc., Br=34.4 per cent.)

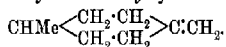


4-Bromo-1-methylcyclohexyl-4-acetic acid melts at 87°, and crystallises from light petroleum, in which it is readily soluble, in well-defined, glistening prisms with truncated ends; it is very readily soluble in methyl alcohol, ether, or benzene.

Similar experiments were made on the action of hydrobromic acid on *d*- and *l*-1-methylcyclohexylidene-4-acetic acids, and resulted in both cases in the production of an optically inactive bromo-acid identical in all respects with that obtained from the externally compensated unsaturated acid.

We have previously prepared this substance by the action of fuming hydrobromic acid on 4-hydroxymethylcyclohexyl-4-acetic acid (Trans., 1908, **93**, 1082); Wallach (*Annalen*, 1907, **353**, 312) made the same substance by treating the 1-methylcyclohexylidene- $\Delta^3$ -acetic acid of Marckwald and Meth with hydrobromic acid.

4-Methylene-1-methylcyclohexane,

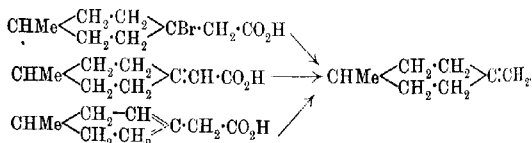


Finely divided 4-bromo-1-methylcyclohexyl-4-acetic acid dissolves readily in sodium carbonate solution, but the liquid gradually clouds, and an oil separates; the change occurs rapidly when the solution is warmed at 40°. The oil is extracted with ether, the ethereal extract carefully dried and evaporated, and the residue distilled; the whole quantity passes over at 122°, and the following results were obtained on analysis. (Found, C=87.1; H=12.8. Calc., C=87.3; H=12.7 per cent.)

Density at 19°/19°=0.7923. Refractive index:  $n_D = 1.4465$  at 18°.

The molecular refraction:  $M_D = 37.06$ ; calculated,  $M_D = 36.43$ .

There can be no doubt that this hydrocarbon is 4-methylene-1-methylcyclohexane, and identical with the compound which Wallach obtained (*Annalen*, 1906, **347**, 345; 1909, **365**, 267) by the slow distillation both of 1-methylcyclohexylidene-4-acetic acid and of 1-methyl- $\Delta^3$ -cyclohexene-4-acetic acid, intramolecular change taking place in the latter case:

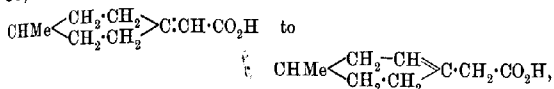


The hydrocarbon obtained by Wallach exhibited properties which are practically identical with those obtained by us, namely, boiling point, 122°; density at 20°/20°=0.7920;  $n_D = 1.4450$  at 20°;

molecular refraction\*,  $M_D = 36.96$ . The decomposition of 4-bromo-1-methylcyclohexyl-4-acetic acid by means of sodium carbonate solution appears to furnish an almost quantitative yield of pure 4-methylene-1-methylcyclohexane, and is therefore doubtless the best method at present available for the preparation of this interesting hydrocarbon.

*Conversion of 1-1-Methylcyclohexylidene-4-acetic Acid into  
dl-1-Methyl-Δ<sup>3</sup>-cyclohexene-4-acetic Acid.*

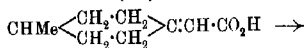
It has been already shown (Trans., 1909, 95, 1802) that 1-methylcyclohexylidene-4-acetic acid can be converted into the 1-methyl-Δ<sup>3</sup>-cyclohexene-4-acetic acid of Marckwald and Meth (Ber., 1906, 39, 1171 and 2404). In this reaction:



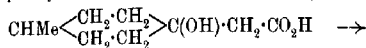
a centrosymmetric substance is converted by intramolecular change into one containing an asymmetric carbon atom. Having previously studied this interconversion with the aid of the externally compensated 1-methylcyclohexylidene-4-acetic acid, we proceeded to examine the reaction which occurs when one of the optically active components of the above acid is converted. *l*-1-Methylcyclohexylidene-4-acetic acid (3 grams) is heated with sulphuric acid (24 grams), water (6 grams), and alcohol (30 c.c.) on the water-bath for three hours. After adding water and extracting with ether, the ethereal solution is washed with dilute sodium carbonate solution, which removes a small quantity of an acid, dried, and evaporated, the residue being left in a vacuum desiccator over sulphuric acid for some hours. The ester thus obtained was found to be optically inactive, and, on hydrolysis, yielded a syrupy acid, which soon crystallised; the oily impurity was removed by contact with porous earthenware, and a satiny, crystalline mass remained, which melted at 37–40° (compare Marckwald and Meth, Ber., 1906, 39, 1174). This consisted of 1-methyl-Δ<sup>3</sup>-cyclohexene-4-acetic acid, and was found to be optically inactive.

It is thus proved that the optically active 1-methylcyclohexylidene-4-acetic acid undergoes optical inversion during conversion into the isomeride which contains an asymmetric carbon atom. The formation of the latter externally compensated acid probably takes place in accordance with the following scheme. The elements of water are first taken up at the double linking in the optically active 1-methylcyclohexylidene-4-acetic acid (I), yielding the saturated 4-hydroxy-acid (II), of which the molecular configuration is not

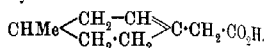
enantiomorphous; this substance then loses water, with the formation of the externally compensated 1-methyl- $\Delta^3$ -cyclohexene-4-acetic acid (III):



(I.) Optically active.



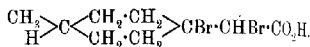
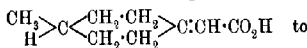
(II.) Potentially inactive.



(III.) Externally compensated.

*Addition of Bromine to 1-Methylcyclohexylidene-4-acetic Acid.*

A reaction of more profound interest than those studied above is provided in the addition of bromine to 1-methylcyclohexylidene-4-acetic acid; the change involved is expressed by the transition:



For if, considering the carbon atoms (1) to (8) as lying in the same plane as the hydrogen atom (c), and the carbon and hydrogen atoms (9) and (a), as numbered on p. 1511, as lying in a plane approximately perpendicular to the foregoing (compare *Trans.* 1909, **95**, 1792), the modes in which the molecular configuration can take up bromine are traced, it will be seen that the two configurations of 1-methylcyclohexylidene-4-acetic acid can give rise to four stereoisomeric dibromides. In order clearly to understand the mode of production of two stereoisomeric dibromides from each of the optically active 1-methylcyclohexylidene-4-acetic acids, it is convenient to examine models of the various molecular configurations involved; these are depicted in the accompanying plate. When the unsaturated optically active 1-methylcyclohexylidene-4-acetic acid, of which the molecular configuration is depicted in Fig. 1, becomes saturated by the addition of bromine, two products may result. For if, in the diagrammatic formula on p. 1511 the (b) and (a) methyl radicle and hydrogen atom are supposed to lie respectively above and below the plane of the paper containing the centres of the carbon atom present in the hexamethylene ring, the two bonds of the ethylenic linking (4:7) must also lie above and below that plane. Either of these two components of the double bond may disappear owing to the substance becoming saturated by the addition of bromine, and, according as the lower



FIG. 1.

FIG. 4.

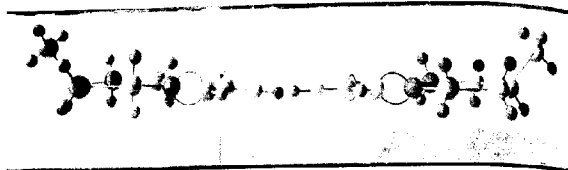


FIG. 2.

FIG. 5.

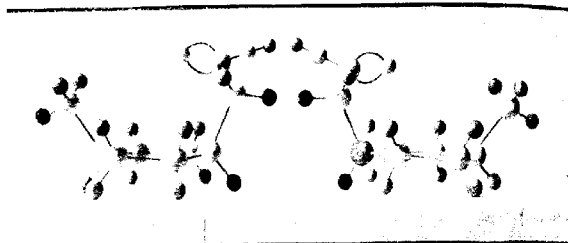
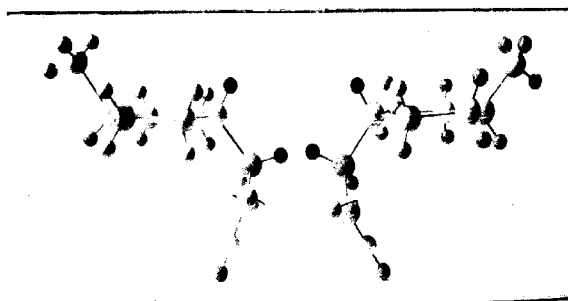


FIG. 3.

FIG. 6.



[To face p. 1517.]

the upper bond is regarded as dissolved, the carbon atom (7) will, in the dibromide, bend towards the methyl group or towards the hydrogen atom ( $\alpha$ ). The configuration (Fig. 1) of the unsaturated acid will thus lead to the production of two dibromides, which differ in configuration as indicated in Figs. 2 and 3; similarly, the unsaturated acid (Fig. 4) enantiomorphously related to that shown in Fig. 1 will give rise to two dibromides (Figs. 5 and 6), of which the molecular configurations are enantiomorphously related respectively to those depicted in Figs. 2 and 3. The small spheres representing bromine atoms in Figs. 2, 3, 5, and 6 are painted black.

The original 1-methylcyclohexylidene-4-acetic acid only possesses one element of molecular asymmetry, and the dibromide produced herefrom only contains one asymmetric carbon atom in the molecule; the two enantiomorphously related modifications of the unsaturated acid should yield, however, four optically active isomerides of the saturated dibromide. For purposes of classification, therefore, it is convenient to regard the dibromides as exhibiting two elements of asymmetry, namely, a centroasymmetry exhibited by the right-hand part of the configurations of Figs. 1, 2, and 3, and an asymmetry of the carbon atom (7), as is shown in Figs. 2 and 3. It is thus evident that another new type of optically active substance may be realised, a type which combines the elements of centroasymmetry discussed above, as one asymmetric centre, with an asymmetric carbon atom, as a second asymmetric centre.

In view of the complexity of isomerism of the dibromides as indicated by the above discussion of the theoretical possibilities, it becomes of importance to investigate carefully the action of bromine on both the externally compensated and the optically active 1-methylcyclohexylidene-4-acetic acids in order to ascertain with certainty how many isomerides are actually produced during the addition of bromine. As the result of this study it has been found that the externally compensated and the optically active isomerides each yield two stereoisomeric dibromides. This accords entirely with the theoretical anticipations; as, however, we have at present no method for discriminating between configurations (2) and (3), it is convenient to distinguish the two stereoisomeric dibromides merely as the  $\alpha$ - and  $\beta$ -isomerides in the present paper.

*$\alpha$ - and  $\beta$ -4-Dibromo-dl-1-methylcyclohexyl-4-acetic Acids.*

The action of bromine on *dl*-1-methylcyclohexylidene-4-acetic acid was studied in a variety of different ways, and the best results were obtained when the following conditions were observed.

The solution of the acid in a little dry chloroform is cooled to  $-10^{\circ}$ , and gradually mixed with one molecular proportion of bromine dissolved in two volumes of chloroform; addition takes place readily. On exposing the product on a clock-glass to a current of air with frequent stirring, the syrupy residue soon commences to crystallise, and, after remaining for several days in the ice-chest, the mass, which still retains a considerable amount of oil, is left in contact with porous earthenware until quite dry. The colourless residue, consisting of a mixture of the  $\alpha$ - and  $\beta$ -dibromides, is then digested with a large amount of light petroleum (b. p.  $40-50^{\circ}$ ), which dissolves most of the  $\alpha$ -isomeride and any oily impurity, and the residue, after several crystallisations from light petroleum (b. p.  $70-80^{\circ}$ ), yields  $\beta$ -4-dibromo-*dl*-1-methylcyclohexyl-4-acetic acid as a hard, crystalline crust:

0.1471 gave 0.1863  $\text{CO}_2$  and 0.0610  $\text{H}_2\text{O}$ .  $\text{C}=34.5$ ;  $\text{H}=4.6$ .

0.2577 „ 0.3076 AgBr.  $\text{Br}=50.8$ .

$\text{C}_9\text{H}_{11}\text{O}_2\text{Br}_2$  requires  $\text{C}=34.4$ ;  $\text{H}=4.5$ ;  $\text{Br}=50.9$  per cent.

$\beta$ -4-Dibromo-*dl*-1-methylcyclohexyl-4-acetic acid melts at  $145-146^{\circ}$ , and is readily soluble in ethyl acetate, methyl alcohol, or warm benzene, but very sparingly so in light petroleum. It separates from benzene in well defined, elongated prisms, and from light petroleum in crusts consisting of groups of colourless needles.

For the purpose of separating the  $\alpha$ -isomeride, the light petroleum mother liquors separated from the  $\beta$ -compound are allowed to evaporate, the semi-solid residue left in the ice-chest for several days, and then placed in contact with porous earthenware. After absorption of the oily impurity, the residue is crystallised several times from light petroleum; in this way the  $\alpha$ -isomeride can be separated, although possibly not quite completely, from the  $\beta$ -compound described above:

0.1427 gave 0.1794  $\text{CO}_2$  and 0.0581  $\text{H}_2\text{O}$ .  $\text{C}=34.3$ ;  $\text{H}=4.5$ .

0.3014 „ 0.3584 AgBr.  $\text{Br}=50.6$ .

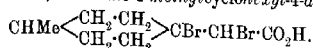
$\text{C}_9\text{H}_{11}\text{O}_2\text{Br}_2$  requires  $\text{C}=34.4$ ;  $\text{H}=4.5$ ;  $\text{Br}=50.9$  per cent.

$\alpha$ -*dl*-1-Methyl-4-dibromocyclohexyl-4-acetic acid melts at about  $106^{\circ}$ , and separates, when its solution in light petroleum is allowed to evaporate spontaneously, as a crust composed of characteristic nodular masses of colourless needles. It is readily soluble in alcohol, ethyl acetate, chloroform, or benzene, but rather sparingly so in light petroleum (b. p.  $40-50^{\circ}$ ).

A long series of experiments on the addition of bromine to *dl*-1-methylcyclohexylidene-4-acetic acid showed that the above two isomerides were apparently the only products formed during the reaction; these  $\alpha$ - and  $\beta$ -isomerides are doubtless represented by the

molecular configurations depicted in Figs. 2 and 3. As is shown below, each is an externally compensated compound, so that the one represents the enantiomorphously related configurations 2 and 5, and the other the similarly related configurations 3 and 6.

*d*- and *l*- $\alpha$ - and  $\beta$ -Dibromo-1-methylcyclohexyl-4-acetic Acids,



The addition of bromine to the *d*- and *l*-1-methylcyclohexylidene-4-acetic acids, and the subsequent isolation of the products, is carried out in the same manner as that adopted in the treatment of the externally compensated acid. Using pure *d*- and *l*-acid having the specific rotatory power  $[\alpha]_D +$  and  $-81.1^\circ$ , two optically active isomeric dibromides are obtained from each optically active acid; the optically active dibromides thus produced are the components of the externally compensated  $\alpha$ - and  $\beta$ -dibromides described above. On repeatedly crystallising the bromination products of the optically active acids from light petroleum, the  $\beta$ -isomeride is obtained as a substance sparingly soluble in light petroleum, and crystallising therefrom in hard crusts composed of small, glistening prisms; it melts at  $154^\circ$ , and on crystallising together equal quantities of the  $\beta$ -isomerides produced from the enantiomorphously related acids, the externally compensated  $\beta$ -dibromide melting at  $145$ – $146^\circ$  results. The optically active  $\beta$ -dibromo-1-methylcyclohexyl-4-acetic acids separate on slow evaporation of their solutions in ethyl acetate in lustrous, transparent crystals; Mr. A. Hutchinson, M.A., has kindly provided the following report, based upon measurements made by Mr. A. F. Hallimond on crystals of the  $\beta$ -isomeride.

Crystal System: Tetragonal.  $a:c=1:1.452$ .

Forms observed:  $m\{110\}$  and  $p\{111\}$ .

The crystals are of prismatic habit, terminated at each end by the pyramid faces,  $p$ , and are 4–5 mm. long and 1–2 mm. thick; only two crystals were available for measurement, and the prism faces were too rounded for reliable measurements to be obtained from them. Each crystal, however, afforded a good value for the angle between the two pyramid planes (111) and (111). The most reliable of these values was  $128^\circ 4'$ , and from this the axial ratio quoted above was calculated. One of the crystals immersed in a liquid of refractive index 1.6, and viewed along the optic axial direction in convergent polarised light, exhibited a perfect uniaxial interference figure; no indication of circular polarisation was observed, nor could any evidence of the existence of a uniterminal



axis be obtained. In default of any evidence to the contrary, these crystals may therefore be provisionally assigned to the holohedral class of the tetragonal system. No cleavage was observed, the crystals breaking with a conchoidal fracture. The specific gravity, determined by the suspension method in Thoulet's solution, was found to be 1.827 at 21°, compared with water at 4°. The inclination of the pyramid planes was such as to permit the determination of both indices of refraction by the method of minimum deviation. The values obtained from the first crystal ( $pp=128^{\circ}4'$ ) for sodium light were  $\mu_o=1.612$  and  $\mu_e=1.584$ ; the second crystal ( $pp=127^{\circ}46'$ ) gave very similar values, namely,  $\mu_o=1.611$  and  $\mu_e=1.586$ .

Although no evidence of enantiomorphous crystal structure was obtained, it can hardly be doubted that these crystals belong to one of the enantiomorphous classes of the tetragonal system (compare Pope, Trans., 1896, 69, 971; Pope and Harvey, Trans., 1901, 79, 828).

The following determinations of rotatory power were made:

*$\beta$ -Dibromo-1-methylcyclohexyl-4-acetic acid from*

*l*-1-Methylcyclohexylidene-4-acetic acid.      *d*-1-Methylcyclohexylidene-4-acetic acid.

In benzene solutions.

0.2983 gram in 20.05 c.c. at 16° in a 2-dcm. tube.				0.4545 gram in 30 c.c. at 17° in a 4-dcm. tube.			
	Hg <sub>green</sub> .	Hg <sub>yellow</sub> .	Na <sub>yellow</sub> .		Hg <sub>green</sub> .	Hg <sub>yellow</sub> .	Na <sub>yellow</sub> .
$\alpha$ ...	-0.87°	-0.75°	-0.73°	$\alpha$ ...	+1.76°	+1.52°	+1.47°
$[\alpha]$ ...	-29.2	-25.2	-24.5	$[\alpha]$ ...	+29.0	+25.1	+24.3
Dispersion: $Hg_{green}/Na_{yellow}=1.192$ . $Hg_{yellow}/Na_{yellow}=1.029$				Dispersion: $Hg_{green}/Na_{yellow}=1.193$ . $Hg_{yellow}/Na_{yellow}=1.033$ .			
0.6011 gram in 20.05 c.c. at 16° in a 2-dcm. tube.				0.9015 gram in 30 c.c. at 17° in a 4-dcm. tube.			
$\alpha$ ...	-1.69°	-1.48°	-1.43°	$\alpha$ ...	+3.39°	+2.94°	+2.86°
$[\alpha]$ ...	-28.2	-24.7	-23.9	$[\alpha]$ ...	+28.2	+24.5	+23.8
Dispersion: $Hg_{green}/Na_{yellow}=1.180$ . $Hg_{yellow}/Na_{yellow}=1.034$ .				Dispersion: $Hg_{green}/Na_{yellow}=1.185$ . $Hg_{yellow}/Na_{yellow}=1.029$ .			

It is very difficult to obtain the  $\beta$ -dibromides in a state of high purity, and on recrystallising the *d*-isomeride several times from benzene the following values, slightly higher than the foregoing, were obtained for the rotatory powers:

0.4996 gram, made up to 30 c.c. with benzene, gave the values +1.96°, +1.71°, and +1.65° for the angle  $\alpha$  with mercury green, mercury yellow, and sodium yellow light respectively in 4-dcm. tubes at 17°; the respective specific rotatory powers,  $[\alpha]$ , are thus +29.6°, +25.6°, and +24.3°, and the rotatory dispersions are, for  $Hg_{green}/Na_{yellow}=1.218$ , and  $Hg_{yellow}/Na_{yellow}=1.053$ .

Whilst the specific rotatory powers of this substance in benzene solution are moderately large and of the normal character, the

value for  $H_{g\text{green}}$  being greater than that for  $H_{g\text{yellow}}$ , and the latter, in turn, greater than that for  $N_{a\text{yellow}}$ ; it is interesting to notice that the compound gives much lower values in ethyl acetate solution, and that in this solvent the dispersions are abnormal. The following determinations show that the specific rotatory powers for  $H_{g\text{green}}$  and for the  $D$ -line are practically identical, whilst the value for  $H_{g\text{yellow}}$  is appreciably smaller.

*l*- $\beta$ -Dibromo-1-methylcyclohexyl-4-acetic acid.

*d*- $\beta$ -Dibromo-1-methylcyclohexyl-4-acetic acid.

In ethyl acetate solutions.

1.0951 gram in 30 c.c. at 16°.			0.5306 gram in 30 c.c. at 16°.		
$H_{g\text{green}}$	$H_{g\text{yellow}}$	$N_{a\text{yellow}}$	$H_{g\text{green}}$	$H_{g\text{yellow}}$	$N_{a\text{yellow}}$
$\alpha$ ... -0.34°	-0.27°	-0.34°	$\alpha$ ... +0.16°	+0.14°	+0.17°
$[\alpha]_{D_{20}}$ ... -2.3	-1.9	-2.3	$[\alpha]_{D_{20}}$ ... +2.3	+2.0	+2.4

The optically active  $\alpha$ -dibromo-1-methylcyclohexyl-4-acetic acids are much more readily soluble in light petroleum than are their  $\beta$ -isomerides; in view of the small quantities of material at our disposal and the difficulties encountered in the purification, we have only prepared the  $\alpha$ -dibromide of *l*-1-methylcyclohexylidene-4-acetic acid in sufficient quantity for determination of the rotatory powers. The *d*- and *l*-isomerides separate from light petroleum in hard nodules, composed of colourless needles, which melt at 102°; their specific rotatory powers are opposite in sign to those of the parent acids.

1- $\alpha$ -Dibromo-1-methylcyclohexyl-4-acetic acid.

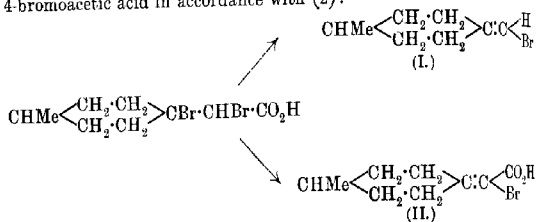
0.3015 gram, made up to 20.05 c.c. with benzene at 16°, in a 2-dcm. tube.				
$H_{g\text{green}}$	$H_{g\text{yellow}}$	$N_{a\text{yellow}}$	$H_{g\text{green}}/N_{a\text{yellow}}$	$H_{g\text{yellow}}/N_{a\text{yellow}}$
$\alpha$ ... +0.31°	+0.28°	+0.26°	1.20	1.08
$[\alpha]_{D_{20}}$ ... +10.3	+9.3	+8.6		
0.6104 gram, made up to 20.05 c.c. with benzene at 16°, in a 2-dcm. tube.				
$\alpha$ ... +0.58°	+0.51°	+0.46°	1.25	1.10
$[\alpha]_{D_{20}}$ ... +9.5	+8.4	+7.6		
0.9986 gram, made up to 30 c.c. with ethyl acetate at 16°, in a 4-dcm. tube.				
$\alpha$ ... +0.66°	+0.57°	+0.46°	1.25	1.10
$[\alpha]_{D_{20}}$ ... +4.9	+4.3	+3.9		

It is very remarkable that although the  $\alpha$ -isomeride resembles the  $\beta$  compound in giving much smaller specific rotatory powers in ethyl acetate than in benzene solution, the former shows about the same rotatory dispersion in the two solvents, whilst the latter exhibits quite abnormal dispersion in ethyl acetate solution. On crystallising together equal quantities of the *d*- and *l*- $\alpha$ -isomerides, the product is found to melt at 105–106°, the melting point of the externally compensated substance.

The fact, which we have now demonstrated, that, in accordance with the indications of theory, the two original centrosymmetric substances yield four optically active dibromides, each of which is

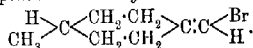
a pure optically active compound, shows that the centroasymmetric structure is possessed of great configurational stability, and can be caused to undergo change in a perfectly definite manner without the occurrence of any optical inversion. It is possible, however, further to extend the work which leads to this conclusion, and to pass from the optically active dibromides, the optical activity of which is associated partly with centroasymmetry and partly with the presence of an asymmetric carbon atom, back again to substances of the purely centroasymmetric type.

Two changes of this kind are at once seen to be possible. On warming the dibromo-1-methylcyclohexyl-4-acetic acids with sodium carbonate solution, they should lose hydrogen bromide and carbon dioxide, giving 1-methyl-4-bromomethylenecyclohexane in accordance with (1), whilst on heating with concentrated potash they should lose hydrogen bromide and yield 1-methylcyclohexylidene-4-bromoacetic acid in accordance with (2):



Both these reactions can be caused to proceed quantitatively, and both, when carried out with the pure optically active  $\alpha$ - or  $\beta$ -dibromides, yield pure optically active centroasymmetric products.

*Externally Compensated 1-Methyl-4-bromomethylenecyclohexane,*



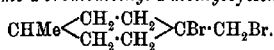
When the solution of the externally compensated modification of either  $\alpha$ - or  $\beta$ -1-dibromo-1-methylcyclohexane-4-acetic acid in sodium carbonate solution is slightly warmed, it rapidly clouds, and the required bromo-hydrocarbon separates as a heavy oil. For the preparation of the substance in quantity, it is convenient to warm the crude product of the bromination of *dl*-1-methylcyclohexylidene-4-acetic acid with excess of sodium carbonate solution, and to distil the whole in a current of steam. The bromo-hydrocarbon, which is readily volatile with steam, is extracted with ether, the extract dried, evaporated, and the residue submitted to fractional distillation:

0.2165 gave 0.2179 AgBr. Br=42.7.

C<sub>8</sub>H<sub>13</sub>Br requires Br=42.4 per cent.

*dl*-1-Methyl-4-bromomethylenecyclohexane distils at 112—113° under 50 mm. or at 128° under 100 mm. pressure, and, when rapidly heated in small quantities under ordinary pressure, distils at 192° without profound decomposition. It has a pungent odour somewhat resembling that of *isoamyl* bromide; its stability is shown by the fact that it is only very slowly decomposed by boiling with sodium ethoxide in alcoholic solution. The chloroform solution of the compound readily absorbs one molecular proportion of bromine at -10°; some hydrogen bromide is, however, eliminated, and, after evaporation of the chloroform, the residual oil could not be caused to crystallise.

4-Bromo-4-bromomethyl-1-methylcyclohexane,

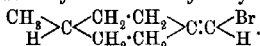


On shaking *dl*-1-methyl-4-bromomethylenecyclohexane with fuming hydrobromic acid, saturated at 0°, it becomes converted into a very heavy oil. On distillation under reduced pressure most of the substance passes over at 120—125°/25 mm., but the appended analysis indicates that some decomposition with evolution of hydrogen bromide takes place under these conditions:

0.1571 gave 0.2092 AgBr. Br=56.6.

C<sub>8</sub>H<sub>14</sub>Br<sub>2</sub> requires Br=59.2 per cent.

*d*- and *l*-1-Methyl-4-bromomethylenecyclohexane,



The  $\alpha$ - and  $\beta$ -isomerides, either of *d*- or *l*-methylcyclohexylidene-4-acetic acid, yield the same product on treatment with sodium carbonate solution under the conditions specified above; the resulting bromo-hydrocarbon is a heavy oil with a pungent odour, which boils at 112—113°/50 mm.

The following determinations of rotatory power were made:

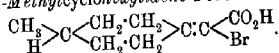
<i>d</i> -1-Methyl-4-bromomethylenecyclohexane dissolved in light petroleum at 16° in 4-dcm. tubes.				<i>l</i> -1-Methyl-4-bromomethylenecyclohexane dissolved in light petroleum at 16° in 4-dcm. tubes.			
3.0051 grams in 30 c.c.				3.0579 grams in 30 c.c.			
Hg <sub>green</sub> .	Hg <sub>yellow</sub> .	Na <sub>yellow</sub> .		Hg <sub>green</sub> .	Hg <sub>yellow</sub> .	Na <sub>yellow</sub> .	
$\alpha$ .....	-23.79°	-20.97°	-20.19°	$\alpha$ .....	+24.10°	+21.27°	+20.43°
$[\alpha]$ ...	-50.37	-52.34	-50.39	$[\alpha]$ ...	+59.11	+52.17	+50.18
Mean dispersions: Hg <sub>green</sub> /Na <sub>yellow</sub> =1.178.				Hg <sub>yellow</sub> /Na <sub>yellow</sub> =1.040.			

In absolute alcoholic solution

1.0158 grams in 30 c.c. at 16° in a 4-dcm. tube.					
$\alpha$ .....	-8.48°	-7.50°	-7.21°	Hg <sub>green</sub> /Na <sub>yellow</sub> .	Hg <sub>yellow</sub> /Na <sub>yellow</sub> .
$[\alpha]$ ...	-62.24	-55.38	-50.4	1.179	1.041.
$[\alpha]$ ...	-117.6	-104.7	-100.6		

It will be seen that during the series of reactions by means of which the replacement of a hydrogen atom by bromine and of the carboxyl group by a hydrogen atom has been effected in the original 1-methylcyclohexylidene-4-acetic acid, the sign of the optical activity has been reversed; at no stage during the series, however, has any indication of optical inversion been obtained. The rotatory dispersions are practically the same, whether light petroleum or ethyl alcohol is used as the solvent.

*d*- and *l*-1-Methylcyclohexylidene-4-bromoacetic Acid,



Pure *l*-α-4-dibromo-1-methylcyclohexyl-4-acetic acid (m. p. 154°,  $[\alpha]_D -24.5^\circ$ ) was stirred into a paste with very little water, mixed with ten parts of 50 per cent. potassium hydroxide solution, and rapidly heated to boiling over a naked flame; in a few seconds the liquid clouded, and, on cooling, a potassium salt separated in quantity. The alkaline liquid was decanted as completely as possible, the salt washed with a little 50 per cent. potassium hydroxide solution, dissolved in water, acidified with hydrochloric acid, and the syrupy acid extracted with ether. After drying and evaporating, a nearly colourless syrup remained, which, when left for some days in the ice-chest and persistently rubbed, ultimately solidified. The crystals were squeezed between two pieces of porous earthenware, and then became perfectly colourless; the material was, however, so readily soluble in organic solvents that it was found impossible to recrystallise the small quantity which we had at our disposal. For the purpose of further purification it was therefore dissolved in light petroleum (b. p. 40–50°), the filtered solution evaporated, and the mass, as soon as crystallisation was nearly complete, rapidly transferred to porous porcelain; this operation was twice repeated, and the substance then analysed:

0.1511 gave 0.1201 AgBr. Br = 33.8.

$\text{C}_9\text{H}_{13}\text{O}_2\text{Br}$  requires Br = 34.3 per cent.

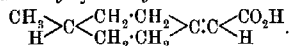
1-Methylcyclohexylidene-4-bromoacetic acid melts approximately at 50°; the identity of our product was controlled by the following titration: 0.3128 gram of the acid, dissolved in dilute alcohol, required, for neutralisation, 13.5 c.c. of *N*/10-NaOH, whereas this quantity of the monobasic acid,  $\text{C}_9\text{H}_{13}\text{O}_2\text{Br}$ , should neutralise 13.4 c.c.

The following determinations of rotatory power were made with 1-methylcyclohexylidene-4-bromoacetic acid in alcoholic solutions, 4-dcm. tubes being used:

0.4906 gram in 30 c.c. at 19°.				0.8900 gram in 30 c.c. at 16°.			
	Hg <sub>green</sub> .	Hg <sub>yellow</sub> .	Na <sub>yellow</sub> .		Hg <sub>green</sub> .	Hg <sub>yellow</sub> .	Na <sub>yellow</sub> .
$\alpha$ .....	-0.81°	-0.72°	-0.68°	$\alpha$ .....	-1.44°	-1.26°	-1.22°
$[\alpha]$ .....	-12.4	-11.0	-10.4	$[\alpha]$ ....	-12.1	-10.6	-10.8
$[M]$ ...	-28.9	-25.6	-24.2	$[M]$ ...	+28.2	-24.7	-24.0
Mean dispersions: Hg <sub>green</sub> /Na <sub>yellow</sub> =1.18.				Hg <sub>yellow</sub> /Na <sub>yellow</sub> =1.02.			

On repeating this preparation, using *d*- $\beta$ -dibromo-1-methylcyclohexyl-4-acetic acid, a product was obtained which gave the specific rotatory power  $[\alpha]$  for the Hg<sub>green</sub> line of +12.8°. It is thus proved that the  $\alpha$ - and  $\beta$ -dibromides derived from one optically active 1-methylcyclohexylidene-4-acetic acid yield the same optically active 1-methylcyclohexylidene-4-bromoacetic acid under the conditions prescribed above.

*d*-1-Methylcyclohexylidene-4-acetic Acid,



A curious numerical relation has been observed between the molecular rotatory powers of the centroasymmetric substances with which we are now concerned; this made it important to obtain more complete data than those given in our previous papers for the rotation constants of 1-methylcyclohexylidene-4-acetic acid. The following determinations were made with a highly purified specimen of the *d*-acid: 0.2608 gram was made up to 30 c.c. with absolute alcohol, and examined in a 4-dcm. tube at 18°:

	Hg <sub>green</sub> .	Hg <sub>yellow</sub> .	Na <sub>yellow</sub> .	Hg <sub>green</sub> /Na <sub>yellow</sub> .	Hg <sub>yellow</sub> /Na <sub>yellow</sub> .
$\alpha$ .....	+3.33°	+2.61°	+2.82°	1.181	1.032
$[\alpha]$ .....	+95.8	+83.7°	+81.1		
$[M]$ ...	+147.6	+129.0	+125.0		

The following table states the molecular rotatory powers in alcoholic solution of the centroasymmetric compounds described in the present paper.

*Molecular Rotatory Powers.*

	Hg <sub>green</sub> .	Hg <sub>yellow</sub> .	Na <sub>yellow</sub> .
(1) <i>d</i> -R: $\begin{array}{c} \text{H} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{H} \end{array}$	0	0	0
(2) <i>d</i> -R: $\begin{array}{c} \text{H} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{CO}_2\text{H} \end{array}$	+147.6°	+129.0°	+125.0°
(3) <i>d</i> -R: $\begin{array}{c} \text{Br} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{H} \end{array}$	-117.6	-104.7	-100.6
Algebraic sums of (2) and (3):	+30.0	+24.3	+24.4
(4) <i>d</i> -R: $\begin{array}{c} \text{Br} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{CO}_2\text{H} \end{array}$	+28.9	+25.6	+24.0

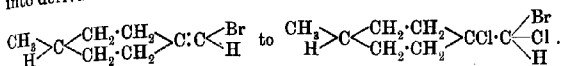
On replacing the lower hydrogen atom in (1) by carboxyl, as in (2), the molecular rotatory power changes from zero to the positive value given under (2). On replacing the upper hydrogen atom in (1) by bromine, the molecular rotatory powers similarly change from zero to the negative values given under (3). On making both of the above substitutions simultaneously, the effect on the original rotatory power of zero of (1) is, within the limits of experimental error, found to be the algebraic sum of the two substitutions performed separately. The algebraic sums of the molecular rotatory powers of (2) and (3) are thus very nearly equal to the corresponding molecular rotatory powers of (4). The angular changes in molecular rotatory power brought about by these substitutions are roughly proportional to the atomic or molecular volumes of the substituting groups.

*The Relation between Optical Activity and Asymmetry of Atomic Environment.*

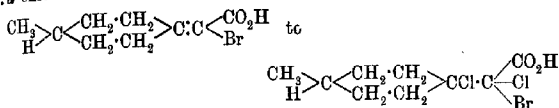
It has been frequently suggested that asymmetry of a carbon atom is not alone a sufficient indication of optical activity, but that a certain complexity of molecular constitution must necessarily accompany enantiomorphism of molecular configuration if stable optical activity is to result. This suggestion is, of course, based on the view that if the asymmetry of a particular atom depends on the attachment to that atom of three or four single and different atoms, isomeric change may well determine the optical inversion of any optically active individual component of the synthetic material. The only positive experimental evidence opposed to the above suggestion is apparently the observation of Swarts (*Bull. Acad. Roy. Belg.*, 1896, [iii], **31**, 28) to the effect that fluorochlorobromoacetic acid,  $\text{CFCIBr-CO}_2\text{H}$ , can be caused, by crystallisation with strychnine or cinchonine, to yield a component exhibiting fugitive optical activity. Much negative evidence in support of the suggestion mentioned is, however, available (Pope and Read, *Trans.*, 1908, **93**, 794).

Obviously, the difficulty of obtaining a solution of the problem suggested above is largely due to the difficulty of synthesis of the materials required for the experimental work. These difficulties, however, are to a large extent removed by the discovery of the optically active centrosymmetric compounds. We are now able to prepare from optically active centrosymmetric substances compounds of which the optical activity is associated with the presence of a single asymmetric carbon, the asymmetry being determined by the attachment of one complex group and three single atoms to one particular carbon atom.

Thus, the optically active centroasymmetric 1-methyl-4-bromomethylenecyclohexanes are, by treatment with chlorine, convertible into derivatives of the simple asymmetric character just premised:

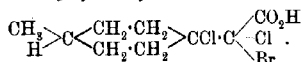


Similarly, the optically active 1-methylcyclohexylidene-4-bromoacetic acids should take up chlorine to yield a dichloride which contains an asymmetric carbon atom attached to a bromine and a chlorine atom:



It must be noted that it is not to be anticipated that, starting from a pure optically active 1-methylcyclohexylidene-4-bromoacetic acid or 1-methyl-4-bromomethylenecyclohexane, a single product should be obtained; the respective dichlorides furnish a case of isomerism identical in character with that of the *l*-dibromo-1-methylcyclohexyl-4-acetic acids, and should consequently be formed as mixtures of an  $\alpha$ - and a  $\beta$ -isomeride, just as described in connexion with the latter acids.

1,4-Chloro-1-methylcyclohexyl-4-chlorobromoacetic Acid,



Pure *l*-1-methylcyclohexylidene-4-bromoacetic acid is dissolved in three volumes of glacial acetic acid, the solution cooled to  $-5^\circ$ , and a slow stream of chlorine passed until addition is complete and the liquid has acquired a yellow colour. During the whole operation the apparatus is enveloped in black paper, and, after remaining overnight in the ice-chest, the product is dissolved in ether, thoroughly washed with water, dried, and the ether evaporated at a low temperature. The almost colourless residue was left over phosphoric oxide and sulphuric acid in a vacuum desiccator for two days, and then analysed:

0.963 gave 0.1453 AgCl, AgBr.  $\text{Cl}_2\text{Br} = 49.1$ .

$\text{C}_8\text{H}_{12}\text{O}_2\text{Cl}_2\text{Br}$  requires  $\text{Cl}_2\text{Br} = 49.6$  per cent.

This dichlorobromo-acid is a viscid syrup, which on long preservation in the ice-chest becomes partially crystalline; it is feebly laevorotatory, as is indicated by the appended determinations.

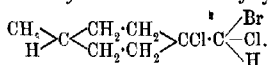


0.9485 gram, made up to 25 c.c. with absolute alcohol, and examined in a 4-dm. tube at 17°, gave the following values:

	Hg <sub>green</sub>	Hg <sub>yellow</sub>	Na <sub>yellow</sub>	Hg <sub>green</sub> /Na <sub>yellow</sub>	Hg <sub>yellow</sub> /Na <sub>yellow</sub>
$\alpha$ .....	-0.26°	-0.17°	-0.16°	1.26	1.07
$[\alpha]$ ...	-1.32	-1.12	-1.05		

The small values obtained for the specific rotatory powers of this substance, together with the fact that we have been unable to treat the compound by methods which would ensure its purity, might lead to three suggestions which would account for the slight optical activity observed. It may be suggested (1) that the optical activity is due to the presence of 1-methylcyclohexylidene-4-bromoacetic acid which had escaped addition of chlorine, or (2) that during the addition of the halogen considerable optical inversion had occurred. The suggestion (1) must, however, be abandoned because the rotatory dispersions of the dichloride, namely, 1.26 and 1.07, are appreciably different from those for the original unsaturated bromo-acid, namely, 1.18 and 1.02; it is thus impossible to attribute the optical activity to the presence of unaltered 1-methylcyclohexylidene-4-bromoacetic acid. With regard to suggestion (2) it should be remarked that no optical inversion was observed during the addition of bromine to the optically active 1-methylcyclohexylidene-4-acetic acids, and that the product, in the latter cases, consisted of a mixture of the  $\alpha$ - and  $\beta$ -isomerides which exhibited specific rotatory powers of opposite signs. It is thus scarcely to be doubted (3) that the *l*-4-chloro-1-methylcyclohexyl-4-chlorobromoacetic acid with which we are now dealing is a mixture of the  $\alpha$ - and  $\beta$ -*lævo*-isomerides exhibiting rotatory powers of opposite signs; that two isomerides of the  $\alpha$ - and  $\beta$ -type are present is, of course, strongly indicated by the fact that the substance slowly becomes partially crystalline.

*d*-4-Chloro-1-methyl-4-chlorobromomethylcyclohexane,



The *d*-1-methyl-4-bromomethylenecyclohexane used in the preparation of the above compound was the *lævorotatory* modification obtained by the action of sodium carbonate on the dibromides of *d*-1-methylcyclohexylidene-4-acetic acid; the latter acid exhibited  $[\alpha]_D + 81.1^\circ$ .

The solution of this bromo-hydrocarbon in acetic acid is cooled to  $-5^\circ$ , carefully protected from light, and saturated with dry chlorine; after remaining for twenty-four hours in the ice-chest,

water is added, the heavy oil extracted with ether, the ethereal solution washed thoroughly with water and sodium carbonate solution, dried, and evaporated. An oil is thus obtained which distils almost completely at 171–173°/35 mm., only a small quantity of a residue of higher boiling point being left in the distilling flask; after redistillation the material was analysed:

0.1086 gave 0.2005 AgCl, AgBr.  $\text{Cl}_2\text{Br}=58.7$ .

$\text{C}_9\text{H}_{13}\text{Cl}_2\text{Br}$  requires  $\text{Cl}_2\text{Br}=58.1$  per cent.

This dichlorobromo-hydrocarbon is a colourless oil, which does not appear to undergo any decomposition when distilled under diminished pressure; it has the pungent odour characteristic of substances of similar composition:

1.0710 gram, made up to 30 c.c. with absolute alcohol at 17°, and examined in a 4-dcm. tube, gave the following results:

	Hg <sub>green</sub> .	Hg <sub>yellow</sub> .	Na <sub>yellow</sub> .	Hg <sub>green</sub> /Na <sub>yellow</sub> .
$\alpha$ .....	+0.055°	+0.05°	+0.05°	
$[\alpha]$ ...	+0.39	+0.35	+0.35	1.10

The discussion given above of the cause of the optical activity of the last compound described is immediately applicable to the present one; the optical activity cannot be attributed to the presence of unchlorinated substance, because the parent compound exhibits a specific rotatory power opposite in sign to that of the saturated halogen derivative of the hydrocarbon. In this, as in the preceding, case the low specific rotatory power is doubtless due to the preparation being a mixture of a dextro- and a *levo*-rotatory  $\alpha$ - and  $\beta$ -isomeride.

Our thanks are due to Dr. John Read for the care with which he has carried out much of the experimental work involved in the present paper.

THE CHEMICAL DEPARTMENT,  
THE UNIVERSITY, MANCHESTER.

THE CHEMICAL LABORATORY,  
THE UNIVERSITY, CAMBRIDGE.

CLXXIII.—*Some Reactions of Gum Kino.*

By JOHN LIONEL SIMONSEN.

DURING the course of a number of researches on Indian products which are in progress in these laboratories, the attention of the author was directed to the constituents of the gum kino obtained from *Pterocarpus Marsupium*.

Kino was first subjected to a careful investigation by Etti (*Ber.*, 1878, 11, 1879), who stated that when kino was heated with dilute hydrochloric acid, in addition to a deep red phlobaphen, kino red, a crystalline substance could be extracted with ether. To this substance he gave the name kinoin, and the formula  $C_{14}H_{12}O_6$ . He, however, isolated only a very small quantity of this compound, and did not subject it to any careful examination beyond suggesting that it contained a methoxy-group and readily passed into kino red. The only other mention of this substance in the literature is a short note by A. G. Perkin and Yoshitake (*Trans.*, 1902, 81, 1173) at the conclusion of their investigations on catechin, in which they state that they isolated kinoin, and tested its tinctorial properties.

Considerable doubt as to the existence of this substance was caused by the work of E. White (*Pharm. J.*, 1903, [iv], 16, 676), who stated that he was quite unable to obtain any kinoin from kino obtained from Malabar.

Since it seemed possible to the author that kinoin might be closely related to catechin, it was thought worth while to subject kino to thorough re-investigation. The kino which was used in this research was of undoubted authenticity, and it was obtained for the author by Dr. J. R. Henderson, Superintendent of the Madras Museum, to whom he wishes to express his thanks for his kind assistance.\*

As a preliminary step, Etti's experiments (*loc. cit.*) were very carefully repeated, using the quantities and the conditions recommended by him. In no experiment was it found possible, however, to isolate any trace of kinoin. In some experiments a very small amount of a crystalline substance was obtained, which showed all the properties of catechol. The presence of catechol is readily explained by the fact that crude gum kino itself always contains a small quantity of this substance, which may be extracted from

\* In investigating natural products, the age of the substances is a matter of considerable importance. In the author's preliminary experiments, kino of unknown age was used, but in the later experiments freshly collected and undried gum was employed. It may perhaps be mentioned that in this case no difference in the results obtained was noticed.

it with ether. Since hydrolysis with dilute hydrochloric acid did not result in the production of any kinoin, experiments were instituted with other hydrolytic agents. In no case, however, was any kinoin obtained.

Kino itself, when dried, is a deep red, brittle, amorphous solid. Its properties, especially with regard to its tanning power, have been very carefully studied by Hooper (*Indian Agric. Ledger*, 1901, No. 11). Since it was found impossible to purify this gum in any way, attention was directed to its derivatives. Kino is readily methylated when treated with methyl sulphate and potassium hydroxide.\* The methyl ether thus obtained is an almost colourless, amorphous powder, which could not be crystallised. It was purified by precipitation from alcohol, and gave on analysis figures agreeing with the formula  $C_{15}H_{11}O_4(OMe)_3$ . In order to obtain some confirmation of these figures, the acetate was also prepared in the usual manner, and was isolated as an amorphous, brown powder. On analysis it gave figures closely agreeing with those required by the formula  $C_{15}H_{11}O_4(OAc)_3$ . At my request Mr. Ramaswami Krishna Iyer, M.A., kindly made a molecular-weight determination of kino methyl ether, since the general properties of these substances indicated that they must have a higher molecular weight than that required by the simple formula  $C_{15}H_{11}O_4(OH)_3$  for kino. The results of this determination (see p. 1533) show clearly that kino methyl ether has a molecular weight at least twice that required by the simplest formula. Whether it is possible, however, to place much reliance on this result is doubtful, since it is probable that the ether exists in solution as a colloid. This determination is of some interest, since it has been shown recently by Iijin (*J. pr. Chem.*, 1910, [ii], 82, 422) that the molecular weight of tannin must be much higher than is suggested by the work of Nierenstein.

When kino methyl ether is oxidised in the cold with potassium permanganate, the only product of the oxidation is veratric acid. It was stated by Hlasiwetz (*Annalen*, 1865, 134, 122) that when kino was fused with potassium hydroxide, it yielded protocatechuic acid and phloroglucinol. The production of veratric acid supported this statement, but no trace of a phloroglucinol derivative could be isolated. The presence of such a nucleus in kino was further rendered doubtful by the fact that on repeating the fusion of kino with potassium hydroxide only protocatechuic acid and catechol could be isolated, there being no indication of any trace of phloroglucinol.

\* The author can confirm the statement of White *loc. cit.* with reference to the absence of a methoxy-group in kino.

An interesting result was obtained when kino itself or the phlobaphen, kino red, was oxidised with dilute nitric acid. When the oxidation is carried out under the conditions described in the experimental part of this paper (p. 1534), the product consists of a mixture of oxalic acid and ammonium quadroxalate. The formation of this ammonium salt during the course of an oxidation in which excess of acid is present is extremely remarkable. The ammonia can obviously only be due to the reduction of some of the nitric acid, and its formation is a proof of the extraordinary reducing power of kino. Ammonium quadroxalate is a salt of very great stability, and is not readily decomposed by acids, since it may be crystallised from concentrated hydrochloric acid, and is not acted on by concentrated nitric acid at 100°. It seems doubtful if it can have the normal structure, and experiments are in progress with the view of elucidating this point.

#### EXPERIMENTAL.

Although numerous attempts were made to purify the crude gum, it was found quite impossible to obtain it in a crystalline form and free from inorganic contamination. It showed all the properties ascribed to it by Hooper (*loc. cit.*), and behaved in the usual manner with tannin reagents.

#### *Kino Methyl Ether.*

In carrying out the methylation of kino, the following method was found, after numerous trial experiments, to give the most satisfactory results. Kino (15 grams) was dissolved in alcohol, and methyl sulphate (19 grams) was added. To this mixture potassium hydroxide (9 grams) dissolved in water (10 c.c.) was added all at once. In a short time the mixture became very hot, and the reaction was controlled by cooling with cold water. After some time the same amounts of methyl sulphate and potassium hydroxide were added, and when all reaction had ceased, the solution was diluted, and the amorphous solid (15 grams) which separated, collected and well washed with water.

The crude kino methyl ether obtained in this manner was purified by repeated precipitation from alcohol with water, when it was found to be an almost colourless, amorphous powder, which could not be crystallised. It was quite free from ash, and two distinct preparations gave the following results on analysis, after drying at 110°:

0.1912 gave 0.437  $\text{CO}_2$  and 0.0999  $\text{H}_2\text{O}$ .  $\text{C}=62.3$ ;  $\text{H}=5.8$ .

0.1561 „ 0.3533  $\text{CO}_2$  „, 0.0767  $\text{H}_2\text{O}$ .  $\text{C}=61.7$ ;  $\text{H}=5.5$ .

0.1288 „ 0.2633  $\text{AgI}$ .  $\text{MeO}=26.9$  per cent.

$\text{C}_{15}\text{H}_{11}\text{O}_4(\text{OMe})_3$  requires  $\text{C}=62.1$ ;  $\text{H}=5.7$ ;  $\text{MeO}=26.7$  per cent.

*Kino methyl ether* does not melt at  $300^\circ$ , and is readily soluble in most organic solvents. It is insoluble in alkalis, and its alcoholic solution gives no colour with ferric chloride. It dissolves in concentrated sulphuric acid with a purple-red colour.

A determination of its molecular weight by the cryoscopic method, using naphthalene as a solvent, gave the following result:

0.374, in 25.4 naphthalene, gave  $\Delta t$  0.126.  $\text{M.W.}=818$ .

$(\text{C}_{18}\text{H}_{20}\text{O}_7)_2$  requires  $\text{M.W.}=696$ .

The question as to the value which can be attached to this result has already been discussed (p. 1531).

#### *Acetylkino.*

In preparing this substance, kino (5 grams) was mixed with acetic anhydride (15 grams) and anhydrous sodium acetate (3 grams), and heated for about an hour on the sand-bath. During the heating the kino passes into solution, and, after cooling, the deep red reaction-mixture was poured into water, when the acetylkino separated out as a brown powder.

*Acetylkino*, which, like kino methyl ether, could not be obtained crystalline, was purified by repeated precipitation from acetic acid solution with water. By this means it was obtained as a pale brown powder, readily soluble in most solvents, and showing no characteristic colour reactions. For analysis it was dried at  $110^\circ$ , two distinct preparations being used. The acetyl group determination was made by A. G. Perkin's method:

0.1329 gave 0.2335  $\text{CO}_2$  and 0.0571  $\text{H}_2\text{O}$ .  $\text{C}=58.2$ ;  $\text{H}=4.8$ .

0.132 „ 0.2823  $\text{CO}_2$  „, 0.0578  $\text{H}_2\text{O}$ .  $\text{C}=58.3$ ;  $\text{H}=4.9$ .

0.1519 „ 0.0631  $\text{C}_2\text{H}_4\text{O}_2$ .  $\text{C}_2\text{H}_4\text{O}_2=41.5$ .

$\text{C}_{15}\text{H}_{11}\text{O}_4(\text{O}\cdot\text{CO}\cdot\text{CH}_3)_3$  requires  $\text{C}=58.3$ ;  $\text{H}=4.6$ ;

$\text{C}_2\text{H}_4\text{O}_2=41.7$  per cent.

#### *Action of Hydrochloric Acid on Kino.*

In carrying out these experiments, Etti's method (*loc. cit.*) was used. Kino (50 grams) was mixed with dilute hydrochloric acid (100 grams), and heated to boiling on the sand-bath. The kino passes into solution, and in a short time the whole liquid is filled with a bright red, somewhat gelatinous mass consisting of kino red. After boiling

for half an hour, the hot solution was filtered, cooled, and after saturation with ammonium sulphate, the red solution was extracted with ether. On removing the ether, a small quantity of an oil was obtained, which crystallised, and was found to consist of catechol. No trace of kinoin could be obtained, although the experiment was repeated numerous times, using different conditions. Careful examination also proved the absence of any sugar, showing that kino is not glucosidic in character.

*Fusion of Kino with Potassium Hydroxide.*

Kino (5 grams) was gradually added to molten potassium hydroxide (50 grams) containing a little water. When all the kino had been added, the temperature was raised to 190—210°, and finally for a few minutes to 250°. After cooling, the deep brown fusion was dissolved in water, hydrochloric acid was added until the solution was just acid, and the solution extracted with ether, the ether well washed with sodium hydrogen carbonate to remove acids, dried, and evaporated, when an oil was obtained. This oil partly solidified, and the solid was drained on porous porcelain, and found to consist of catechol. Sufficient of the oily phenol could not be obtained for identification, but no trace of phloroglucinol was detected.

The sodium hydrogen carbonate solution containing the acid was acidified, and extracted with ether, when, on removing the ether, a solid was obtained, which, after crystallisation from water, melted at 197—198°, and was identified as protocatechuic acid.

*Oxidation of Kino Methyl Ether.*

In carrying out this oxidation, kino methyl ether (10 grams) was suspended in dilute sodium carbonate solution, and shaken in the cold with potassium permanganate until a permanent pink colour was obtained. After filtering from manganese dioxide, the solution, which had a strong odour of vanillin, was concentrated on the water-bath, acidified, and after being saturated with ammonium sulphate, extracted with ether. On removing the ether, a viscous oil remained, which rapidly solidified. After draining on porous porcelain, it was crystallised from hot water, when it melted at 178—179°, and showed all the properties of veratric acid. (Found. C=59.2; H=5.5. Calc., C=59.3; H=5.5 per cent.)

*Oxidation of Kino and Kino Red with Nitric Acid.*

It has already been mentioned (p. 1531) that when kino or kino red is oxidised with dilute nitric acid, the double salt of oxalic

acid, ammonium quadroxalate is formed. Since the conditions in both oxidations were the same, only the oxidation of kino red is described.

Kino red (5 grams) was mixed with nitric acid (10 per cent.) (30 c.c.), and allowed to remain in the cold with constant shaking. The mixture gradually becomes warm, and in order to prevent the reaction becoming too vigorous it is necessary to cool the flask in running water. After remaining in the cold for twelve hours, the reaction was completed by warming on the water-bath for five to six hours. The solution was filtered from some unattacked kino red, and the deep brown filtrate concentrated on the water-bath, when, on cooling, ammonium quadroxalate separated in large, hexagonal rhombohedra (yield 1 gram). The mother liquor on concentration gave a small quantity of oxalic acid.

Ammonium quadroxalate, which was purified by crystallisation from water, melts and decomposes at  $130^{\circ}$ , and crystallises with two molecules of water of crystallisation. (Found, C=20.5, 20.2; H=4.8, 4.7; N=6.3. Calc., C=20.6; H=4.7; N=6.0 per cent.) That this substance was ammonium quadroxalate was confirmed by direct comparison with a specimen prepared from oxalic acid and ammonium oxalate.

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MADRAS.

#### CLXXIV.—*Synthesis of Derivatives of Thioxanthone.* *Part III. 1:4-Dihydroxythioxanthone.*

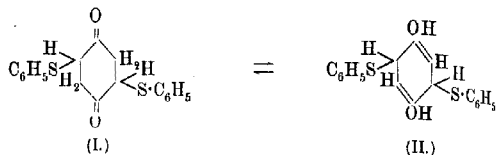
By HANS THACHER CLARKE and SAMUEL SMILES.

In addition to the various general methods now available (Meyer, *Ber.*, 1909, **42**, 1134; Davis and Smiles, *Trans.*, 1910, **97**, 1290; Marsden and Smiles, this vol., p. 1353; Smiles, *Proc.*, 1910, **26**, 342) for the synthesis of derivatives of thioxanthone, another has been devised which is especially suitable for the production of dihydroxy-derivatives. The experiments described in the present paper have been carried out in illustration of this method, and the synthesis of 1:4-dihydroxythioxanthone is described.

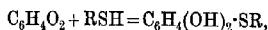
The process may be accomplished in two stages, of which the first consists of the union of *o*-thiolbenzoic acid with a quinone. The interaction of quinones and aromatic mercaptans has been studied by Tröger and Eggert (*J. pr. Chem.*, 1896, [ii], **53**, 482), who found that an excess of phenyl mercaptan reacts with *p*-benzoquinone,



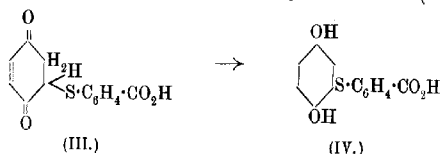
giving an additive product of the composition  $C_6H_4O_2 \cdot 2C_6H_5SH$ . Posner (*Annalen*, 1904, **336**, 85), in re-investigating this substance, showed that addition of the mercaptan takes place at the ethylenic groups of the quinonoid nucleus (as in I); but since the substance appeared to behave in the hydroxylic form (II), he represented it by the following tautomeric scheme:



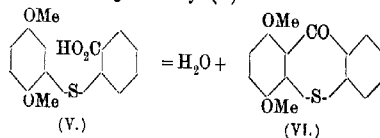
More recently the interaction of equimolecular proportions of *p*-benzoquinone and sulphydric derivatives has been described in patent literature (Badische Anilin- und Soda-Fabrik, D.R.P. 175070). Thus monothio-derivatives are obtained according to the equation:



where R represents an acid group, either organic or inorganic. We find that a similar interaction occurs between *o*-thiolbenzoic acid and quinones. According to the interpretation given by Posner to this type of reaction, it is evident that the product from that acid and *p*-benzoquinone would be the dihydro-derivative (III):

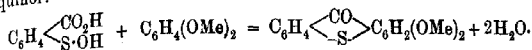


but since the substance obtained behaves according to the hydroxylic structure, we prefer to represent it as the derivative of quinol (IV), which is evidently produced from the dihydro-compound by intramolecular rearrangement. Thus, when the substance is methylated in alkaline solution, it yields a dimethyl derivative, which must be formulated as containing methoxyl (V):



for on treatment with cold sulphuric acid, this yields 1:4-dimethoxythioxanthone (VI), the latter being identical with the product

obtained from *o*-dithiobenzoic acid and the dimethyl ether of quinol:



The parent substance—1:4-dihydroxythioxanthone (VI)—is readily obtained from the dihydroxy-sulphide (IV) by treatment with dehydrating agents. This compound is deep orange, and furnishes crimson salts with alkaline hydroxides; but it is of little value as a dyestuff, since it does not form lakes, and the alkali salts are very readily oxidised.

The synthetical method which is illustrated in this paper appears to be capable of wide, although not universal, application.

#### EXPERIMENTAL.

##### *2'-Carboxy-2:5-dihydroxydiphenyl Sulphide,* $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{S} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}.$

Five and a-half grams of *p*-benzoquinone were dissolved in about 150 c.c. of cold glacial acetic acid, and, while the mixture was constantly shaken, a thin paste made of 7.7 grams of *o*-thiolbenzoic acid with the same medium was added. After the lapse of twenty-four hours a small quantity of *o*-dithiobenzoic acid was removed by filtration from the red-coloured liquid; the latter was then evaporated on the water-bath with continual addition of water until the bulk of the acetic acid was expelled. When a suitable concentration was reached, sulphurous acid was added, and the liquid was filtered while hot. On cooling the solution a crystalline mass of the required acid was deposited. This was recrystallised from hot water, from which the substance separated in small, colourless prisms, melting at 199°:

0.0955 gave 0.2066  $\text{CO}_2$  and 0.0358  $\text{H}_2\text{O}$ .  $\text{C}=59.0$ ;  $\text{H}=4.1$ .

$\text{C}_{15}\text{H}_{10}\text{O}_4\text{S}$  requires  $\text{C}=59.5$ ;  $\text{H}=4.1$  per cent.

The acid is readily soluble in cold ether or alcohol, and sparingly so in cold water. This substance exhibits a characteristic behaviour when its aqueous solution is warmed with concentrated aqueous ferric chloride. The red, crystalline precipitate which is then formed appears to be a ferric salt of the corresponding quinone; but analysis showed that it is of complex composition.

##### *2'-Carboxy-2:5-dimethoxydiphenyl Sulphide,* $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{S} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}.$

A solution of one molecular proportion of the dihydroxy-acid in methyl alcohol which contained an excess of sodium methoxide

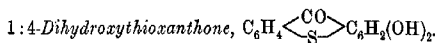
# 1538 SYNTHESIS OF DERIVATIVES OF THIOXANTHONE. PART III.

was mixed with about three molecular proportions of methyl sulphate. The mixture was subsequently heated on the water-bath, and finally the alcohol was removed by evaporation. The residue was treated with cold aqueous sodium hydroxide, and the insoluble portion was removed by filtration. The filtrates were acidified, and the precipitate was collected and well washed with warm water. The product was finally recrystallised from alcohol, when the required acid was obtained in colourless prisms:

0.1056 gave 0.2399 CO<sub>2</sub> and 0.0487 H<sub>2</sub>O. C=61.9; H=5.1.

C<sub>15</sub>H<sub>14</sub>O<sub>4</sub>S requires C=62.0; H=4.8 per cent.

When heated, the substance shrinks at about 190°, and finally melts at 195°.

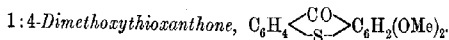


A solution of carboxydihydroxydiphenyl sulphide in sulphuric acid was kept overnight at the atmospheric temperature. It was then poured on crushed ice, when the required substance was precipitated in an impure condition. This was collected, washed with water, and then exhaustively extracted with hot alcohol. When cold, the united extracts deposited dihydroxythioxanthone in the crystalline state; but the material tenaciously retained a considerable quantity of sulphuric acid. The further purification of the product was effected by repeated boiling with water until the acid could no longer be detected in the solution. Finally, the substance was recrystallised from alcohol, when it was obtained in deep orange prisms, which melted at 289°, and were sparingly soluble in hot water or common organic media:

0.1866 gave 0.4388 CO<sub>2</sub> and 0.0524 H<sub>2</sub>O. C=64.1; H=3.1.

C<sub>13</sub>H<sub>8</sub>O<sub>3</sub>S requires C=63.9; H=3.2 per cent.

The alkali salts of this substance are crimson, but, owing to the ease with which they are oxidised in alkaline solution, they were not isolated in a pure condition. Attempts were made by oxidation to obtain the corresponding quinone, but with the three or four oxidising agents employed the products were difficult to purify, and appeared to consist of polyhydroxy-derivatives.



(a) The dimethoxy-derivative of carboxydiphenyl sulphide was treated with sulphuric acid as described above. The product obtained by mixing the acid solution with water was collected, and, after being washed in order to remove excess of acid, was treated

with dilute aqueous sodium hydroxide. The insoluble residue was usually recrystallised from hot alcohol, in which it is moderately soluble.

1:4-Dimethoxythioxanthone forms bright orange prisms, which melt at 195°, and readily dissolve in sulphuric acid, giving a solution of characteristic red colour:

0.1019 gave 0.2460 CO<sub>2</sub> and 0.0405 H<sub>2</sub>O. C=65.8; H=4.4.

C<sub>15</sub>H<sub>12</sub>O<sub>3</sub>S requires C=66.1; H=4.4 per cent.

(b) The condensation of *o*-dithiobenzoic acid and the dimethyl ether of quinol was carried out by the same process as that employed, and elsewhere described, for the synthesis of other thioxanthone derivatives of a similar type (Marsden and Smiles, this vol., p. 1353). In order to obtain good yields it is important to employ a large excess of the quinol ether and to moderate the temperature of condensation. The product was purified in the usual manner, when it was obtained in orange prisms, melting at 194–195°. A mixed melting point showed that the substance was identical with that obtained by the method described in the foregoing paragraph.

In conclusion, we desire to express our thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed the expenses of this research.

THE ORGANIC CHEMISTRY LABORATORY,  
UNIVERSITY COLLEGE, LONDON.

# CLXXV.—Contributions to the Chemistry of the Terpenes. Part IX. The Oxidation of Camphene with Hydrogen Peroxide.

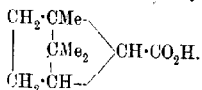
By GEORGE GERALD HENDERSON and MAGGIE MILLEN JEFFS  
SUTHERLAND, B.Sc., Carnegie Research Scholar.

A THIRTY per cent. aqueous solution of hydrogen peroxide was recently used by one of us (Henderson and Boyd, *Trans.*, 1910, **97**, 1659) as an oxidising agent for various cyclic compounds with satisfactory results, and we have now begun to study the action of this reagent on the terpenes, in the hope that its comparatively mild action, under suitable conditions, would not lead to any of these perplexing changes in molecular structure to which the terpenes in general are peculiarly liable. Camphene, which was selected for

the first experiments, was found to undergo oxidation readily when exposed to the action of hydrogen peroxide under the conditions described in this paper, and to yield a mixture containing a number of different oxidation products, some of which were acids, whilst some were neutral compounds. The chief ingredient of the mixture of acids was a saturated monobasic acid of the formula  $C_9H_{16} \cdot CO_2H$ , which was obtained as a crystalline solid, melting at  $95^\circ$ ; much smaller quantities of two other acids, one a crystalline solid which melts at about  $70^\circ$ , and the other an oily liquid which boils at  $153^\circ/20$  mm., were also present. The two latter compounds have not yet been further investigated as their separation is difficult, and the quantity in our hands is unfortunately small. Among the neutral products of oxidation the ketone camphenilone,  $C_9H_8O$ , is present in largest proportion, but in addition to this the mixture contains *isocamphenilanaldehyde*,  $C_9H_{15} \cdot CHO$ , a compound which appears to have the formula  $C_9H_{16}O_2$ , and when heated with phthalic anhydride yields the acid *phthalate* of an alcohol of the formula  $C_9H_{16}O$ , a very small quantity of camphene glycol,  $C_{10}H_{16}(OH)_2$ , and a trace of a crystalline solid, which melts at about  $69^\circ$ .

The acid of melting point  $95^\circ$ , for which we propose the name *camphylic acid*, was converted into its *chloride*,  $C_9H_{15} \cdot COCl$ , which, when heated with bromine, gave the *chloride of bromocamphylic acid*,  $C_9H_{14}Br \cdot COCl$ . The free acid,  $C_9H_{14}Br \cdot CO_2H$ , obtained by treatment of its chloride with water, yielded *hydroxycamphylic acid*,  $C_9H_{14}(OH) \cdot CO_2H$ , when heated with aqueous sodium carbonate. The hydroxy-acid did not yield a ketone on oxidation with lead peroxide, and therefore does not contain a tertiary hydroxyl group in the  $\alpha$ -position, as is the case with the isomeric camphenylic acid.

When heated with acetic anhydride, camphylic acid is transformed into the isomeric *isocamphenilanic acid*, which was first obtained by the action of hot strong nitric acid on camphenilanic acid (Bredt and Jagelki, *Annalen*, 1900, **310**, 112). The two latter acids are almost certainly stereoisomerides, and there is little doubt that their constitution may be represented by the formula:



Since camphylic acid cannot have this formula, its conversion into *isocamphenilanic acid* must be accompanied by a molecular rearrangement. The constitution of camphylic acid has not been determined, but probably its nucleus is different from that of

camphene. If, as appears to be the case, the molecule of camphene contains the group  $>\text{C}:\text{CH}_2$ , oxidation would lead to the formation of camphenilanic (or *isocamphenilanic*) acid, and not of camphylic acid, unless a certain rearrangement took place under the influence of the oxidising agent.

*iso*Camphenilanic acid itself is not found among the products of the oxidation of camphene by hydrogen peroxide, although its aldehyde is present in considerable quantity. This leads to the conclusion that hydrogen peroxide is not an active oxidising agent for aldehydes, at least under the conditions which prevailed in our experiments. *iso*Camphenilanaldehyde is very similar in properties to camphenilanaldehyde, with which it is isomeric, and which was obtained by Bredt and Jagelki (*loc. cit.*) as the sole product of the oxidation of camphene with chromyl chloride. On exposure to air, however, the former is oxidised rapidly and completely to *isocamphenilanic* acid (m. p.  $118^\circ$ ), whilst the latter yields camphenilanic acid. Both aldehydes appear to form the same semicarbazone, and this compound must really be a derivative of the *iso*aldehyde, because when it is decomposed by treatment with dilute acids it is the latter that is regenerated.

The compound  $\text{C}_9\text{H}_{16}\text{O}_2$  is a remarkable one, if its composition be that indicated by the results of analysis, but at present we cannot do more than record its behaviour. It does not react with alkalis, or semicarbazide hydrochloride, or phenyl carbimide, or benzoyl chloride, but is readily oxidised to camphenilone by potassium permanganate, and, as already stated, can be converted into an alcohol,  $\text{C}_9\text{H}_{16}\text{O}$ , by heating with phthalic anhydride and subsequent hydrolysis of the ester thus produced. The alcohol, which was obtained in crystals, melting at  $94^\circ$ , is apparently isomeric with camphenilol, the secondary alcohol corresponding with camphenilone, but its constitution has not been determined.

Camphenilone has already been obtained from camphene in several different ways, but the direct formation of this compound, and of *isocamphenilanaldehyde* and camphene glycol, through the action of hydrogen peroxide is of interest, because it affords confirmation of the view that the nucleus of each of these substances is the same as that of camphene itself.

We are now engaged in examining the action of hydrogen peroxide on other terpenes, and hope to communicate our results to the Society before long.

#### EXPERIMENTAL.

*Oxidation of Camphene, and Separation of the Acids Produced.*  
A number of preliminary experiments were made in order to

determine the most favourable conditions for oxidation, and the method ultimately adopted was to add the necessary quantity of a 30 per cent. aqueous solution of hydrogen peroxide to a solution of camphene in four times its weight of glacial acetic acid, and to heat the mixture at about  $60^{\circ}$  under a reflux condenser. At this temperature the oxidation of the camphene proceeds slowly, and requires several days for completion, but a higher temperature is not advantageous, for although the reaction is accelerated, there is at the same time considerable loss of hydrogen peroxide through decomposition. If smaller proportions of acetic acid are used, some of the camphene remains intact, even after prolonged heating. The quantity of hydrogen peroxide added was varied in different experiments, but with the sole result that the relative proportions of the oxidation products showed corresponding variations, whilst their nature was not affected. When one molecular proportion of the oxidising agent was used for each molecular proportion of camphene, some of the hydrocarbon escaped oxidation, and only a very small quantity of acids was found among the products. When the proportion of hydrogen peroxide was increased to two or three molecules for each molecule of camphene, the oxidation of the latter was practically complete, and the products contained proportionately larger quantities of acids. On the whole, the best results were obtained by taking three molecules of the peroxide for one molecule of camphene.

The oxidation was judged to be complete when no sublimation of camphene into the tube of the condenser was observed. Sodium carbonate was then added to the liquid, which had acquired a yellow colour, until nearly all the acetic acid was neutralised, and a yellow, oily liquid which separated was extracted by repeated agitation of the mixture with ether. The aqueous solution was acidified with dilute sulphuric acid and thoroughly extracted with ether, and from the ethereal extract a small quantity of acids was obtained. The ethereal solution of the bulk of the oxidation product was washed with water, dried, and the oily liquid which remained after removal of the ether by distillation was warmed on the water-bath with aqueous sodium carbonate until no more passed into solution. The alkaline liquid, when cool, was shaken several times with ether in order to remove the neutral substances which remained undissolved, which constituted the greater part of the whole product, and was then acidified with dilute sulphuric acid. The precipitated acids, together with the small quantity which remained in solution, were extracted with ether, and, after the extract had been washed with water and dried, were recovered on distilling off the ether in the form of an oily liquid,

which gradually became crystalline. The separation of the acids present in this mixture was very troublesome and tedious because of their great solubility in all the usual organic solvents, but ultimately, by repeated recrystallisation from light petroleum and subsequently from methyl alcohol, we succeeded in isolating three acids. The least soluble portion, which constituted the bulk of the mixture, was a solid melting at 93–94°; the second fraction was also a solid, melting at about 70°, and the most easily soluble part was an oily liquid, which boils at 153°/20 mm. Only small quantities of the two latter acids were obtained, and their further examination was postponed from lack of material.

The principal acid,  $C_9H_{15} \cdot CO_2H$ , which may be called *camphyllic acid*, when finally purified by crystallisation from water and from light petroleum successively, melted at 95°. It is extremely easily soluble in alcohol, ether, light petroleum, or other usual organic solvents, very sparingly so in hot, and hardly at all in cold, water, and it has a great tendency to form supersaturated solutions in methyl alcohol or light petroleum. From the latter solvents it crystallises in well developed, colourless, lustrous prisms, which, if formed slowly, may be a centimetre or more in length, and from water or dilute methyl alcohol it separates in delicate needles. It volatilises, but slowly, in a current of steam. Towards bromine or potassium permanganate, it behaves as a saturated compound. When heated on the water-bath with a strongly alkaline solution of potassium permanganate, it is slowly attacked, but no oxidation product other than carbon dioxide was identified. It remains unchanged, even after prolonged heating with nitric acid of concentrations varying from 10 to 50 per cent.:

0.2475 gave 0.6472  $CO_2$  and 0.2169  $H_2O$ .  $C=71.3$ ;  $H=9.8$ .

0.1864 „ 0.4850  $CO_2$  „ 0.1622  $H_2O$ .  $C=71.0$ ;  $H=9.7$ .

$C_{10}H_{16}O_2$  requires  $C=71.4$ ;  $H=9.6$  per cent.

The *sodium* salt separates from water, in which it is readily soluble, in small, colourless prisms. The *ammonium* salt, which also is easily soluble in water, was obtained as a colourless, crystalline powder by passing ammonia into a solution of the acid in dry ether. The *silver* salt,  $C_9H_{15} \cdot CO_2Ag$ , was precipitated as a white, finely crystalline solid on addition of silver nitrate to an aqueous solution of the ammonium salt. It is practically insoluble in water, and darkens slowly when exposed to light. Analysis of this salt confirmed the results obtained with the acid:

0.1432 gave 0.2294  $CO_2$ , 0.0814  $H_2O$ , and 0.0565  $Ag$ .  $C=43.7$ ;  $H=6.3$ ;  $Ag=39.5$ .

$C_{10}H_{15}O_2Ag$  requires  $C=43.6$ ;  $H=5.6$ ;  $Ag=39.3$  per cent.



The first analyses of the acid, which were made on a specimen crystallised from water and not thoroughly dried, gave results which suggested that it might be campholic acid,  $C_{10}H_{18}O_2$ ; moreover, like the latter, the new acid is precipitated, although very slowly, when carbon dioxide is passed through a cold aqueous solution of its sodium salt. In order to settle the point, an attempt was made to prepare the anhydride, which can be obtained from campholic acid. A few grams of the acid were boiled for about an hour under a reflux condenser with a slight excess of acetic anhydride, and the mixture then poured into a large quantity of water, which was subsequently shaken several times with ether. The ethereal solution was washed and dried, the ether removed by distillation, and the residue dissolved in hot light petroleum, in which it was considerably less soluble than the original acid. On cooling the solution, clusters of small, colourless prisms separated which, when dry, melted at  $118^\circ$ , and on treatment with sodium carbonate proved to be crystals of an acid. The melting point of this acid was not changed when it was mixed with *isocamphenilanic* acid,  $C_9H_{15}\cdot CO_2H$ , which also melts at  $118^\circ$ , and analysis confirmed the conclusion that it was nothing but the latter. (Found,  $C=71.5$ ;  $H=9.5$ . Calc.,  $C=71.4$ ;  $H=9.6$  per cent.)

This experiment showed that camphylic acid is transformed into the isomeric *isocamphenilanic* acid when heated with acetic anhydride. No such transformation is brought about when the acid is crystallised repeatedly from alcohol, water, or light petroleum, or when it is heated for hours at  $150^\circ$ , or when it is distilled under diminished pressure.

*Preparation of Bromo- and Hydroxy-camphylic Acids.*—The acid was added in small portions to a mixture of the calculated quantity of phosphorus pentachloride with light petroleum contained in a flask under a reflux condenser, the solution was heated to complete the reaction, and then distilled fractionally under diminished pressure. After the solvent and the phosphoryl chloride had passed over, the *chloride* of the acid,  $C_9H_{13}\cdot COCl$ , distilled at  $110^\circ/17$  mm. It is a colourless, viscous liquid, with a pungent but not unpleasant odour, which fumes in moist air. By heating this compound with a slight excess of bromine in a sealed tube at about  $90^\circ$  for several hours, the *chloride* of the bromo-acid,  $C_9H_{11}Br\cdot COCl$ , was obtained as a heavy, viscous liquid, which, when well stirred with water, was slowly converted into the crystalline *bromocamphylic acid*,  $C_9H_{11}Br\cdot CO_2H$ . The acid was collected, dried, and crystallised, first from methyl alcohol, and then from light petroleum. It forms small, lustrous prisms, melts at  $210^\circ$ .

and is very readily soluble in alcohol or ether, sparingly so in light petroleum, and insoluble in water:

0.2002 gave 0.1524 AgBr. Br = 32.3.

$C_{10}H_{15}O_2Br$  requires Br = 39.4 per cent.

On one occasion, in brominating the chloride of camphylic acid, the temperature was accidentally allowed to rise to about  $200^{\circ}$ . When the product was treated with water a neutral compound, which contained bromine, and a bromo-acid, which melted at  $204-205^{\circ}$ , were obtained. The latter was identified as bromo-isocamphenilanic acid, and it follows that, at the high temperature of the experiment, the chloride of bromocamphylic acid must have been transformed into the chloride of bromo-isocamphenilanic acid.

*Hydroxycamphylic acid*,  $C_9H_{14}(OH) \cdot CO_2H$ , was prepared by heating the bromo-acid for some time with excess of aqueous sodium carbonate, and acidifying the alkaline solution, when cool, with dilute sulphuric acid. The crystalline acid which separated was collected on a filter, and the filtrate was extracted repeatedly with ether in order to obtain the portion that remained in solution. In order to remove a small quantity of resinous matter with which it was contaminated, the acid was converted into its *sodium* salt, which was obtained in colourless prisms when the solution was concentrated. The salt was redissolved in water, in which it is fairly readily soluble, and decomposed by addition of sulphuric acid, and the hydroxy-acid was finally purified by successive crystallisations from water and from light petroleum. From the latter solvent it separates in small, lustrous prisms, which melt at  $245^{\circ}$ . It is very easily soluble in alcohol or ether, fairly so in water or light petroleum:

0.2001 gave 0.4750  $CO_2$  and 0.1622  $H_2O$ . C = 64.7; H = 9.0.

$C_{10}H_{16}O_3$  requires C = 65.2; H = 8.7 per cent.

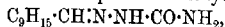
In order to gain more information as to its constitution, a mixture of the hydroxy-acid with a little water and about four times its weight of lead peroxide was distilled in a current of steam. The distillate contained a crystalline, insoluble solid, which was collected and pressed in porous paper. It melts at  $145^{\circ}$ , and has an odour of geraniums; it has the character, not of a ketone, but of an acid. Lack of material prevented further examination of this compound.

*Separation of isoCamphenilanaldehyde*.—The ethereal solution of that portion of the original oxidation product which had not been dissolved by aqueous sodium carbonate was washed with water, dried, and after removal of most of the ether the residual liquid

was mixed with an equal volume of a saturated solution of sodium hydrogen sulphite. Almost at once a "bisulphite compound" began to separate in small, pearly leaflets. After some time this compound was collected, and washed with a very little alcohol, in which it is fairly readily soluble, and with ether. The part of the oily product which had not combined with sodium hydrogen sulphite was extracted from the aqueous filtrate with ether, and treated with fresh quantities of the reagent until no more crystals of the bisulphite compound were formed. The greater proportion of the mixture of neutral oxidation products remained unattacked, and was examined in the manner described below.

*isocamphenilanaldehyde*,  $C_9H_{15}\cdot CHO$ , was obtained by mixing the bisulphite compound with excess of aqueous sodium carbonate, and passing a current of steam through the solution. The aldehyde distilled quickly with steam, and collected in the receiver in soft, crystalline masses. Being extremely easily soluble in alcohol or ether, it is not easily purified by crystallisation from these solvents, and was therefore converted into its semicarbazone, which, after recrystallisation until its melting point was constant, was decomposed by warming with the calculated quantity of dilute sulphuric acid. The liquid was cooled, and the aldehyde collected, well washed with water, and quickly dried by pressure in porous paper. It forms waxy, colourless crystals, which melt at  $69-70^\circ$ , and, like other terpene aldehydes, has a strong, peculiar odour. It is very easily soluble in alcohol, ether, or light petroleum, but insoluble in water, and it readily volatilises in a current of steam. On exposure to air, it oxidises quickly and completely to *isocamphenilanic acid*. Altogether it closely resembles the isomeric *camphenilanaldehyde*.

The semicarbazone of *isocamphenilanaldehyde*,



crystallises from methyl alcohol in small, lustrous prisms, which melt at  $191-192^\circ$ . It dissolves readily in hot, rather sparingly in cold, methyl alcohol:

0.1960 gave 32.8 c.c.  $N_2$  (moist) at  $19^\circ$  and 766 mm.  $N=20.1$ .

$C_{11}H_{19}ON_3$  requires  $N=20.1$  per cent.

The semicarbazone prepared from *camphenilanaldehyde* melts at the same temperature as the compound derived from *isocamphenilanaldehyde*, and so does a mixture of the two compounds, which are thus shown to be identical.

The crystals of the acid produced by exposure of *isocamphenilanaldehyde* to the air was found to melt at  $108-112^\circ$  after pressure in porous paper, and at  $118^\circ$  after crystallisation from light petroleum, from which it separates in clusters of small, colourless

prisms. The melting point was not changed by further crystallisation, and a mixture of the acid with a specimen of *isocamphenilanic* acid, which had been prepared from camphene by *Bredt's* method, also melted at  $118^{\circ}$ . Hence the acid was proved to be *isocamphenilanic* acid, and the aldehyde from which it was formed by spontaneous oxidation in air at the ordinary temperature must be *isocamphenilanaldehyde*.

*Separation of Camphenilone.*—The mixture of neutral oxidation products, which remained after extraction of the acids with sodium carbonate and of *isocamphenilanaldehyde* with sodium hydrogen sulphite, was a viscous liquid, brown in colour, and with a strong odour. On distillation under diminished pressure in an atmosphere of dry carbon dioxide, slight decomposition took place, a small quantity of a dark resinous substance being left in the flask, but the bulk passed over into the receiver. After repeated distillation the mixture was separated into three liquid fractions, which boiled at  $85-88^{\circ}$ ,  $94-100^{\circ}$ , and about  $250^{\circ}$  respectively under 15 mm. pressure.

The chief fraction, that of lowest boiling point, was a colourless, oily liquid, which could not be induced to crystallise, although its characteristic odour suggested that it was the ketone camphenilone,  $C_{15}H_{14}O$ . Analysis indicated that it was a mixture of camphenilone with a little of another substance, and on treatment of a sample with semicarbazide hydrochloride the greater part was quickly converted into a crystalline semicarbazone, but a small quantity of an oily liquid remained unattacked by the reagent. Accordingly, the rest of the fraction was mixed with semicarbazide hydrochloride and potassium acetate, with the necessary quantity of methyl alcohol and water to form a clear solution, enough of the reagent being used to react with the whole of the substance. The semicarbazone, which quickly separated, was collected, and the mother liquor was diluted with water and distilled with steam. The small quantity of oily liquid which distilled with steam was added to the second fraction.

The semicarbazone crystallised from methyl alcohol, in which it is readily soluble, in colourless needles, which melted at  $224-225^{\circ}$ , the melting point of camphenilonesemicarbazone. Analysis gave a corresponding result. (Found,  $N=21.9$ . Calc.,  $N=21.7$  per cent.)

The pure ketone was obtained by warming the semicarbazone with the calculated quantity of dilute sulphuric acid. On cooling, a solid separated, which was collected, washed with water, dried, and crystallised from ether, from which it separated in colourless plates, melting at  $40^{\circ}$ . The ketone had a strong odour, was very easily soluble in alcohol, and readily volatile in steam, and behaved

as a saturated compound towards bromine and towards potassium permanganate. Further proof of its identity with camphenilone was obtained by preparing the oxime, which separated from ether in small, colourless crystals, melting at 105–106°, and very easily soluble in alcohol, chloroform, or light petroleum. These are the properties of campheniloneoxime.

*Separation of the other Neutral Products.*—The quantity of the second fraction (b. p. 94–100°/15 mm.) was much smaller than that of the first. It was first treated with semicarbazide hydrochloride in order to remove any remains of camphenilone, and, after separation from the mother liquor by steam distillation, was fractionated several times under diminished pressure. When purified in this way the product was a colourless, oily liquid with a faint, pleasant odour, which distilled at 94–96°/14 mm. It was analysed with the following results:

0.1754 gave 0.4460  $\text{CO}_2$  and 0.1672  $\text{H}_2\text{O}$ .  $\text{C}=69.3$ ;  $\text{H}=10.5$ .

0.1754 „ 0.4430  $\text{CO}_2$  „ 0.1678  $\text{H}_2\text{O}$ .  $\text{C}=68.9$ ;  $\text{H}=10.6$ .

$\text{C}_9\text{H}_{16}\text{O}_2$  requires  $\text{C}=69.2$ ;  $\text{H}=10.3$  per cent.

This compound is easily oxidised by alkaline potassium permanganate, yielding a substance which has the physical properties of camphenilone, and from which a semicarbazone with the same melting point as camphenilonesemicarbazone was prepared. The compound was apparently indifferent to the action of hot aqueous sodium hydroxide, did not react with phenylcarbimide, and was not affected when treated with benzoyl chloride in presence of pyridine. It was converted into the *acid phthalate* of an alcohol,  $\text{C}_9\text{H}_{16}\text{O}$ , in the following manner. After heating the compound for some time at 150–180° with twice its weight of phthalic anhydride, the product was poured into a beaker containing crushed ice, and sodium carbonate was added until nothing more passed into solution. The alkaline solution was filtered, agitated with ether, acidified with dilute sulphuric acid, and then thoroughly extracted with ether. The ethereal solution was washed and dried, and after removal of the ether the residue was again treated with sodium carbonate, etc., as before. The ester, thus freed from phthalic acid, was finally purified by crystallisation from a mixture of ether and light petroleum, from which it separates in lustrous prisms, which melt at 163–164°. It is very readily soluble in alcohol or ether, very sparingly so in light petroleum or chloroform, and is dissolved by aqueous sodium carbonate with formation of a soluble sodium salt:

0.1134 gave 0.2922  $\text{CO}_2$  and 0.0746  $\text{H}_2\text{O}$ .  $\text{C}=70.3$ ;  $\text{H}=7.3$ .

$\text{C}_{17}\text{H}_{20}\text{O}_4$  requires  $\text{C}=70.8$ ;  $\text{H}=6.9$  per cent.

The alcohol,  $C_9H_{16}O$ , was prepared by warming the ester with aqueous sodium hydroxide, and distilling the liberated alcohol in a current of steam. It collected in the receiver in the form of a white, waxy, crystalline solid, with an odour somewhat like that of camphor, and, when dry, melted at  $94-95^\circ$ . It is very readily soluble in alcohol or ether, and practically insoluble in water:

0.1546 gave 0.4348  $CO_2$  and 0.1632  $H_2O$ .  $C=76.7$ ;  $H=11.7$ .

0.1690 „ 0.4732  $CO_2$  „ 0.1722  $H_2O$ .  $C=76.4$ ;  $H=11.6$ .

$C_9H_{16}O$  requires  $C=77.1$ ;  $H=11.4$  per cent.

This alcohol, although apparently of the same composition, appears to be different from camphenilol, the alcohol corresponding with camphenilone, for the latter melts at  $84^\circ$ , and its acid phthalic ester at  $148^\circ$ . The nature of the compound from which the alcohol was derived has not been determined.

Only a very small quantity was obtained of the highest fraction (b. p. about  $250^\circ/15$  mm.) of the neutral oxidation product. It was an extremely viscous liquid, with a yellow colour, and appeared to contain traces of several compounds. We succeeded in isolating a very small quantity of camphene glycol,  $C_{10}H_{16}(OH)_2$ , and a still smaller quantity of a crystalline compound, which melted at about  $69^\circ$ . This substance forms small, lustrous plates, and is very sparingly soluble in methyl alcohol, fairly readily so in ether.

The preliminary work connected with this research was done by Mr. W. Dickson, A.I.C., who was prevented from completing it by the acceptance of an appointment.

We are indebted to the Carnegie Trust for a grant in aid of the expense of this work, and gladly take this opportunity of expressing our thanks.

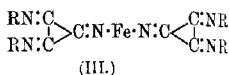
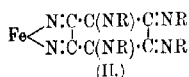
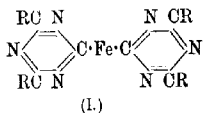
CHEMISTRY DEPARTMENT.  
THE GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

## CLXXVI.—*The Constitution of the Organic Ferrocyanides.*

By ERNALD GEORGE JUSTINIAN HARTLEY.

In two previous communications (Trans., 1910, **97**, 1066 and 1725) the author described some new organic derivatives of hydroferrocyanic acid formed, in the first place, by the action of methyl sulphate on dry potassium ferrocyanide. From the compounds so produced, which are acid and neutral salts of a hexamethylferro-

cyanogen base, by a series of further operations tetramethyl ferrocyanide was prepared. Owing to the uncertainty that still exists as to the constitution of the ferrocyanides, it seemed interesting to study the decomposition products of one or two of these substances in order to throw some light on the subject if possible. The numerous formulæ which have been proposed from time to time for the ferrocyanides may be placed in two classes. The first includes those in which the usual structural conceptions of organic chemistry are adopted:



(I), an example of this class, appears in several standard textbooks of organic chemistry, and was provisionally employed by the author in the papers referred to above. It has apparently been suggested owing to the well-known tendency of the cyanogen radicle to form the stable tricyanogen ring rather than from any specific chemical behaviour of the ferrocyanides.

Further examples are (II) put forward by Friedel (*Compt. rend.*, 1887, **104**, 995), but admitted by him to be not wholly satisfactory, and (III), proposed by Browning (*Trans.*, 1900, **77**, 1238). The latter seems in many respects to represent very well the properties of the ferrocyanides, especially their relationship to the nitroprussides, but it does not appear to have been very widely accepted by organic chemists.

It will be noticed that in (I) the metallic radicles are combined directly with carbon atoms, whilst in (II) and (III) they are attached to nitrogen.

The second class consists of formulæ deduced from various modifications of Werner's so-called co-ordination theory.

It would not be convenient in this communication to enter into a discussion as to the merits of these systems, but reference should be made to two papers by Briggs (*Trans.*, 1908, **93**, 1571, and this vol., p. 1019), in which he applies his own development of the theory to explain the existence of the  $\alpha$ - and  $\beta$ -ferrocyanides described by Locke and Edwards (*Amer. Chem. J.*, 1899, **21**, 193, 413), and the similar  $\alpha$ - and  $\beta$ -ferrocyanides discovered quite recently by himself (*loc. cit.*).

It is not claimed that any definite conclusion can be drawn

from the following experiments as to the general configuration of the molecule, but the arguments in this paper are based on the supposition, favoured by the author, that the ordinary structural theory of organic chemistry can at present be applied to this class of compounds more advantageously than Werner's or any allied system. On this assumption it is demonstrated fairly conclusively that the organic ferrocyanides, at any rate, must be represented by a formula in which the alkyl groups are shown as directly attached to nitrogen. Whether the free acid and its salts are similarly constituted cannot yet be asserted.

It is well known that when metallic ferrocyanides are decomposed by concentrated sulphuric acid, the nitrogen is converted into an ammonium salt, and it seemed probable that the organic ferrocyanides would behave in a similar manner.

The nitrogen would then presumably be found entirely in the form of an ammonium salt if a formula similar to (1) is the correct one, whereas if the methyl groups are attached directly to nitrogen the decomposition should result in the production of some methylammonium derivatives.

In fact, Freund, in his original paper on tetraethyl ferrocyanide, prepared from silver ferrocyanide and ethyl iodide (*Ber.*, 1888, 21, 931), observed that this substance gave off an isocyanide on heating, and that both ethylamine and ammonium sulphates were found in the residue after heating with concentrated sulphuric acid, and these results were confirmed later by Browning (*loc. cit.*).

Experiments have now been carried out on the decomposition, both of tetramethyl ferrocyanide and also of one of the hexamethyl derivatives, namely, hexamethylferrocyanogen dihydrogen sulphate,  $(\text{CH}_3)_6\text{FeC}_6\text{N}_6\text{H}_2(\text{SO}_4)_2$ , since of all the series the latter is most readily obtained pure, and it was hoped that the position of the six methyl groups might be elucidated.

About 0.5 gram of pure tetramethyl ferrocyanide was gradually heated with thirty drops of concentrated sulphuric acid in a platinum crucible until white fumes just began to appear. After keeping at this temperature for several hours the crucible was cooled and the contents examined.

The iron was found to be almost entirely converted into ferric sulphate, which is only very slowly soluble in water when anhydrous. A little water was added, the solution filtered from the iron salt, and a drop of the liquid was tested with platinic chloride, when a precipitate was immediately formed, which was seen under the microscope to consist of a mixture of octahedra and hexagonal plates evidently of ammonium and methylamine platinichlorides respectively.



To the rest of the solution excess of platinic chloride was added, and the precipitate was collected, washed with dilute alcohol, dried at 100°, and the platinum determined:

0.3132 gave 0.1340 Pt. Pt=42.78.

Ammonium platinichloride requires Pt=43.92.

Methylamine platinichloride requires Pt=41.31 per cent.

The percentage of platinum was, as expected, between these two values, but owing to the greater solubility of the methylamine salt it is not possible to calculate the proportion of the two constituents.

A similar experiment was next performed with the hexamethyl compound, the heating being conducted in exactly the same way as above. In order to obtain some evidence as to how far the decomposition is complete under these conditions, the iron was determined in one portion. For this purpose water and a little dilute hydrochloric acid were added to the contents of the crucible, which was allowed to remain until all the ferric salt had dissolved. The iron was then precipitated with ammonia in the usual way, and weighed:

0.6247 gave 0.1040  $\text{Fe}_2\text{O}_3$ . Fe=11.65.

$\text{C}_{12}\text{H}_{20}\text{N}_6\text{Fe}(\text{SO}_4)_2$  requires Fe=11.28 per cent.

Since the iron is not precipitated by ammonia from a solution of the original salt, it is evident that the decomposition was complete, at least so far as detaching the iron from the rest of the molecule.

A second portion of salt was similarly treated, and the platinichloride examined. It was seen under the microscope to consist entirely of hexagonal plates, none of the octahedra of the ammonium salt being observed.

A determination of platinum confirmed this. (Found: Pt=41.47. Calc. for methylamine platinichloride, Pt=41.31 per cent.)

A further experiment was made on the decomposition of the hexamethyl salt with sodium hydroxide solution.

0.2 Gram of salt was heated in a distilling flask with 100 c.c. of 10 per cent. aqueous sodium hydroxide. Decomposition immediately became apparent, a strongly alkaline vapour and an isocyanide being given off, whilst the liquid turned brown, and finally deposited a brownish-black precipitate, probably a mixture of ferrous and ferric hydroxides, since it dissolved in hydrochloric acid, and the solution so obtained gave a blue precipitate, both with potassium ferro- and ferri-cyanide.

The contents of the flask were boiled until about two-thirds of the liquid had passed over, the evolved vapour being condensed in a vessel containing dilute hydrochloric acid, which would convert the isocyanide into an amine salt, and also combine with any free

mine or ammonia if present. When the distillation was stopped, the isocyanide was still being given off in quantity, but it was not possible to continue the boiling without risk of the liquid bumping over. The distillate was evaporated to dryness to remove excess of hydrochloric acid, and the residue was dissolved in a small quantity of water and treated with an excess of platinic chloride and a fair quantity of alcohol.

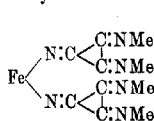
The precipitate, when washed with alcohol and dried, weighed 0.4117 gram, which corresponds with about 72 per cent. of the total nitrogen in the salt taken.

A small portion was examined microscopically, and seen to be free from the octahedra of the ammonium salt.

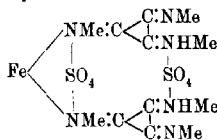
The percentage of platinum again agrees with the ordinary errors of analysis with that required for the methylamine salt (Found, Pt=41.49. Calc., Pt=41.31 per cent.), so that these values, together with the microscopic examination of the platinichlorides, may be taken to prove that no ammonium salt was present.

The fact that the nitrogen in the hexamethyl salt after two completely different methods of decomposition is only found as a methylamine derivative, leads to the conclusion that all the six methyl groups are attached to nitrogen atoms, and consequently in the tetramethyl compound the four methyl groups are probably similarly combined, the two remaining nitrogen atoms in this case forming the ammonium sulphate found after decomposition with sulphuric acid.

Applying Browning's formula to these substances as the best of the ordinary structural formulæ at present available, we get:



Tetramethyl ferrocyanide.

Hexamethylferrocyanogen  
dihydrogen sulphate.

the position of the  $\text{H}_2\text{SO}_4$  in the acid salt being uncertain.

It may finally be suggested that, if the metallic ferrocyanides are constituted similarly to the tetramethyl compound, the  $\alpha$ - and  $\beta$ -forms referred to above may be cases of geometrical isomerism due to nitrogen atoms doubly linked to carbon.

In conclusion, I wish to express my thanks to Lord Berkeley, in whose laboratory these experiments have been carried out, for his help and interest in the work.

FOXCOMBE LABORATORY,  
NR. OXFORD.

CLXXVII.—*The Osmotic Pressure and Conductivity of Aqueous Solutions of Congo-red, and Reversible Membrane Equilibria.*

By FREDERICK GEORGE DONNAN and ALBERT BUCKLEY HARRIS.

THE object of the work described in this paper was to make a somewhat detailed examination of the molecular state of Congo-red in aqueous solution by means of measurements of osmotic pressure and electrical conductivity, and to investigate the effects of certain electrolytes on these properties.\*

Congo-red, the disodium salt of diphenylbisazonaphthylamine-sulphonic acid, is known to possess colloidal properties in aqueous solution. For example, it does not diffuse, or only very slowly, through a membrane of parchment paper, thus rendering the measurement of its osmotic pressure possible with a diaphragm of this sort. W. M. Bayliss (*Proc. Roy. Soc.*, 1909, **81**, B, 345) has made several measurements of the osmotic pressure of Congo-red, his apparatus being a modification of that used by Moore and Roaf (*Bio-Chem. J.*, 1907, **2**, 34). His method consisted in placing Congo-red acid in the osmometer, and adding dilute sodium hydroxide solution to the outside water every twenty-four hours until the latter retained a slight permanent alkalinity. The outside water was then repeatedly changed until no further rise in osmotic pressure occurred. The maximum pressure so obtained was found to vary from 88 to 97 per cent. of the value calculated on the assumption that Congo-red exists in solution as simple, undissociated, and non-aggregated molecules, and from these results Bayliss drew the conclusion that the dye really does exist in solution as simple molecules (M.W. = 696.5). This conclusion, which in itself is rather an unlikely one, will be shown in the course of this paper to be untenable.

Bayliss further showed that the osmotic pressure of Congo-red is lowered by the presence of sodium chloride, sodium hydroxide, and carbon dioxide (carbonic acid).

Since the commencement of the present work † a paper on the osmotic pressure of several colloids has been published by Biltz and von Vegesack (*Zeitsch. physikal. Chem.*, 1909, **68**, 357), among the colloids examined by them being benzopurpurine-4B, a dyestuff

\* This work was primarily undertaken as a preliminary study to a similar investigation of the state of soaps in aqueous solution. The osmotic pressures of these solutions are being at present investigated in this laboratory.

† The publication of the present work has been unfortunately delayed for a year, the experiments having been completed in May, 1910.

early related to Congo-red in chemical composition. From their experiments they concluded that in the absence of foreign electrolytes benzopurpurine-4B exerts a negligibly small osmotic pressure.\* They remarked that during dialysis the solution undergoes a change, the originally bright red solution becoming brownish-black, and they considered this to be simply a mechanical and not a chemical effect, because by heating the dialysed solution (presumably in a glass vessel) the original appearance of the solution was restored. It was assumed by these authors that no hydrolysis could have taken place, because in a particular experiment in which six litres of water were used as outside liquid, no alkali could be detected therein. With regard to the regeneration of the brownish-black dialysed solution by heating, it is quite possible that, even if (partial) hydrolysis had taken place, the alkali taken up from the glass on heating would have been sufficient to reconvert the substance or substances produced by this partial hydrolysis into the original benzopurpurine salt. Thus it is quite easy to convert a dilute solution of the blue Congo-red acid into the bright red solution of the salt by simply boiling the former for some time (less than half an hour) in an ordinary glass beaker.

Again, the fact that no free alkali was detected by Biltz and von Vegesack in the six litres of outside water can easily be accounted for by the large volume of this outside liquid, and the relatively small amount of alkali to be expected.†

It will be shown in the present paper that in this and similar cases hydrolysis, accompanied by the outward diffusion of free alkali, undoubtedly occurs. Indeed, this phenomenon of what we may call "forced membrane-hydrolysis" is an exceedingly interesting and important one, and must always occur to some extent when an electrolyte with a non-dialysing ion (whether kation or anion) is separated by a suitable membrane from pure water.‡

#### EXPERIMENTAL.

For the osmotic pressure measurements described in the present paper, an osmometer was employed which was a modified form of that described by Roaf (*Quart. J. Physiol.*, 1910, 3, 75). A short cylinder of glass 2 cm. long and 3.5 cm. in diameter, provided with

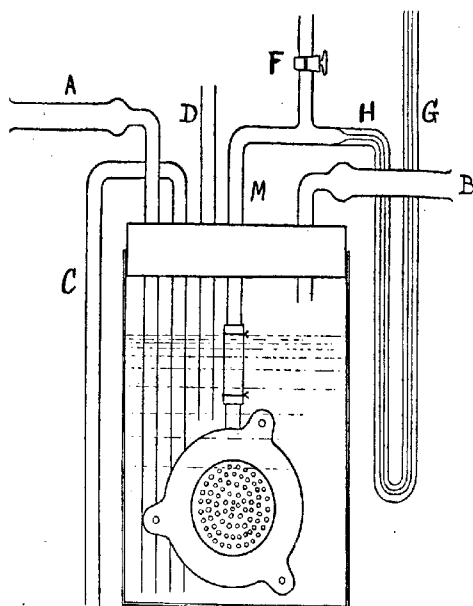
\* Some of the erroneous conclusions arrived at by Biltz and von Vegesack have been corrected in a subsequent paper, which will be discussed later (see p. 1575).

† Moreover, unless every precaution was taken to exclude carbon dioxide, detection of the free alkali which had diffused out by means of phenolphthalein would be very uncertain.

‡ The general theory of the action of membranes in the presence of electrolytes possessing a non-dialysable ion will be discussed in another paper.

a sealed-in side-tube for connexion to the manometer, was closed at either side by parchment-paper diaphragms. These were backed up externally by perforated silver plates, which were tightly pressed against the diaphragms by means of an annular metal framework consisting of two metal rings provided with suitable nuts and screws. A tight joint between the parchment paper and the glass edges of the osmometer vessel was secured by annular rubber washers. The internal volume of the osmometer vessel

FIG. 1.



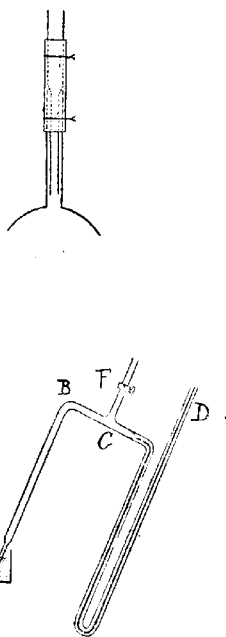
was 20 c.c. Connexion between the latter and the tube leading to the manometer was effected as shown in Fig. 2, the narrowed end of the manometer-tube projecting into the side-tube of the osmometer vessel, the joint being secured by tightly wired rubber pressure-tubing.

The general arrangement is shown in Fig. 1. The osmometer was suspended in a stout cylindrical glass jar of about 1300 c.c. capacity, closed by a large cork, through which passed the tube *M*

leading to the manometer, two soda-lime tubes, *A* and *B*, by means of which the entrance of carbon dioxide is prevented, and two tubes, *C* and *D* (closed by rubber tubes and screw-clips), for changing the liquid external to the osmometer.

In the manometer *HG* (internal diameter 1 mm.) mercury was employed as manometric fluid. The side-tube *F* was employed in the filling and connecting of the manometer, which was carried out as follows. The osmometer vessel, together with the pressure-tubing by means of which it is to be connected to the manometer, is completely filled with the solution to be employed. Mercury is then introduced into the dry inverted manometer through the end *A* (see Fig. 2), the mercury collecting at the bend *B*. By now quickly bringing the manometer into its normal position, keeping the end *D* closed by the finger, the mercury is obtained in the two arms of the capillary pressure gauge without any break, sufficient mercury having been introduced so that in the inclined position shown in Fig. 2 one end of the mercury column can be brought to the position *C*. The end *A* being now dipped into the required solution, the latter is drawn into the manometer by suction at *F*. By now bringing *AB* into a vertical position after closing the tap *F* (the end *A* being still immersed in the solution), the excess of mercury can be run out and the levels brought to any desired position in the pressure-gauge by blowing in at *D*, the mercury which is driven over collecting in the vessel *A*, and being replaced by the solution. The manometer and osmometer having been completely filled are joined together in the manner indicated previously. The modelling material "Plasticene" was found to be a very convenient substance for making the cork of the outer cylindrical jar quite air-tight, a thick layer of this material being spread over the whole top of the cork.

FIG. 2.



After the apparatus has been set up, air, free from carbon dioxide, is drawn for a considerable time through the water in the jar by attaching *B* to a filter pump and *A* to a series of long soda-lime tubes. Throughout all the experiments the presence of carbon dioxide was carefully excluded, for reasons which will appear later.

With regard to the measurement of the osmotic pressure, a correction has obviously to be made for the difference between the level of the outer liquid in the jar and that of the mercury column in the nearer limb of the manometer (the other limb of the manometer was open to the atmosphere). This correction is additive if the water level is below the lower mercury level, and subtractive if the reverse is the case.

*Preliminary Series of Measurements of Osmotic Pressure.*

The first series of measurements was made with solutions of Grubler's Congo-red, which was found to contain about 30 per cent. of sodium chloride. A litre of distilled water, free from carbon dioxide, formed the external liquid. The same general behaviour was observed in all these experiments. The pressure rose quickly at first, the velocity of increase gradually diminishing. After four to five days the pressure attained a maximum, and then began slowly to decrease. On changing the external water, a further rise in pressure occurred, followed by a slow fall. Successive changes of the external water gave rise to the same phenomenon, the increase of pressure becoming, however, rapidly smaller with each successive change of external water. The experiments were carried out at room temperature ( $17^{\circ}$ ), and entrance of carbon dioxide carefully prevented. It was found that the original litre of external water contained nearly all the sodium chloride originally present in the Congo-red, the second litre practically removing the whole of the remainder.

The concentration of the Congo-red in the osmometer (after removal of the sodium chloride) was determined by evaporating 10 c.c. of the cell contents at the end of the experiment, and drying to constant weight at  $110$ – $115^{\circ}$ . The following figures give the results of an osmotic pressure measurement. (Experiment I.):

Time (hours).	Difference of mercury levels (mm.).	Time (hours).	Difference of mercury levels (mm.).
24	88.5	282	125.0
73	105.0	306*	124.0
96	107.5	314	125.0
144	108.0	330*	122.0
234*	105.0	356*	123.0
240	119.0	401	121.0
258	123.0	450	115.0

Indicates a change of the external water.

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Final concentration of Congo-red = 0.578 gram per 100 c.c.

Maximum pressure (corrected for difference of levels) = 136 mm.

(125 + 11).

For single undissociated molecules the osmotic pressure would be:

$$22.4 \times 760 \times \frac{290}{273} \times \frac{5.78}{696.5} = 140 \text{ mm.}$$

The observed value is therefore 97 per cent. of this calculated value.\*

Two other experiments carried out in a similar manner yielded the following final results:

II. Concentration of Congo-red	=	0.387 gram per 100 c.c.
Maximum pressure observed	=	97.0 mm.
Calculated value	=	100.5 mm.
Observed value	=	96.5 per cent. of calculated value.

III. Concentration of Congo-red	=	0.756 gram per 100 c.c.
Maximum pressure observed	=	135.5 mm.
Calculated value	=	136.0 mm.
Observed value	=	95.0 per cent. of calculated value.

These results show a good general agreement with those obtained by Bayliss, in which the Congo-red salt was formed in the osmometer by diffusion of alkali to the blue Congo-red acid. The rise of osmotic pressure observed after each change of external water might be due, as Bayliss supposes, to an increase of "dispersivity" and therefore presumably of osmotic pressure) of the Congo-red solution, as the sodium chloride diffuses out through the parchment diaphragm, or it might be due to the sodium chloride still present in the osmometer exerting an osmotic pressure before it has time to diffuse out. In order to test the latter explanation, experiments (to be described later) have been made with solutions of pure sodium chloride in the osmometer. The general result of these experiments is that the small amount of sodium chloride remaining in the osmometer, even before the first change of external water, that is, after about seven days, could not cause the rise of pressure observed. This argument assumes an equal concentration of sodium chloride inside the osmometer and in the external water. It will be shown later, however, that after a few days the sodium chloride becomes unequally distributed, that is, its concentration in the external water becomes greater than in the osmometer vessel, thus producing an osmotic pressure opposed to that of the Congo-red. When the external water is changed, this counter-pressure is removed, and so a sensible rise of osmotic pressure

\* Throughout this paper, the expression "calculated value" will always refer to that calculated for single undissociated molecules. This method of expressing the results is simply used for the purpose of providing a convenient standard of comparison.



occurs, that is, the true pressure due to the Congo-red present in solution inside the osmometer is observed. That this is probably the true explanation of the phenomenon will appear from the later experiments. It is not necessary, therefore, to suppose that the small concentration of the sodium chloride present in the osmometer exerts any intrinsic action in depressing the osmotic pressure of the Congo-red. This very important matter will be discussed more fully later on.

With regard to the gradual decrease of pressure after a maximum has been attained, this might be attributed to various causes. Sodium chloride might be supposed to be still diffusing slowly from the osmometer, the Congo-red might be undergoing some change of "physical" state, as Biltz and von Vegesack suppose, or a chemical change such as hydrolysis might be occurring. The first hypothesis may be dismissed at once, for the slow fall of pressure occurs long after all the sodium chloride has diffused out of the osmometer.

It may be remarked here that in the foregoing experiments the contents of the osmometer acquire a muddy-brown appearance after about forty-eight hours' dialysis. This appears to be due to the presence of a very fine colloidal suspension. This change in the appearance of the osmometer contents sets in more rapidly at higher temperatures. Moreover, it is found that the muddy-brown solution is unaffected by a small quantity of sodium chloride, whereas a trace of sodium hydroxide suffices to reconvert it into the original bright red solution. We may dismiss, therefore, the hypothesis of Biltz and von Vegesack, and conclude that a slow hydrolysis, accompanied by the diffusion out of sodium hydroxide, and the precipitation in fine, semi-colloidal suspension of some very insoluble substance (perhaps a mixture, or "adsorption-compound," of Congo-red acid, or the acid salt, with the original Congo-red), is occurring. This would give a satisfactory explanation of the gradual fall in osmotic pressure. Were this the case, we should expect to be able to prevent this "membrane-hydrolysis," and so obtain constant osmotic pressures by employing instead of pure water a dilute solution of sodium hydroxide as external liquid. Experiment confirms this conclusion, for the employment of a  $N/800$ -sodium hydroxide solution suffices entirely to prevent the "precipitation" of an 0.5 per cent. solution of Congo-red at 25°, and enables a perfectly definite and constant osmotic pressure to be obtained. These results enable us also to understand why Bayliss found that carbon dioxide exerted a marked action in lowering the osmotic pressure of Congo-red solutions; for the carbonic acid in the external water will combine with the alkali

that diffuses out, and so hasten and increase the hydrolysis and precipitation in the osmometer. The following experiment will serve to confirm this conclusion. Two similar osmometers were filled with the same 0.5 per cent. solution of Grüber's Congo-red. In the case of one osmometer, entrance of carbon dioxide was prevented as described previously. The other osmometer was simply suspended in an open beaker containing a volume of ordinary distilled water equal to the volume of water, free from carbon dioxide, in the protected outer jar of the first osmometer. The osmotic pressure fell, in one case, from 82.5 mm. to 69.5 mm. in seventeen days, whilst in the other case (unprotected osmometer) it fell in the same time from 85.5 to 53.5 mm.

The gradual hydrolysis of Congo-red on dialysis with continued change of the outer water was conclusively proved as follows: 100 c.c. of a 0.5 per cent. solution of Merck's Congo-red were placed in a parchment dialysing tube, which was suspended in a beaker containing a litre of distilled water. This outer water was changed every day. The original Congo-red (Merck's) was found to contain 16.47 per cent. of sodium, showing the presence of a fairly large amount of foreign electrolytes (sodium chloride and sulphate). After four days' dialysis a portion of the solution was evaporated to dryness, and the sodium content of the dry residue determined. This was found to be 6.5 per cent. (theoretical value for Congo-red, 6.6 per cent.). After three weeks' dialysis the sodium content of the dried residue obtained on evaporation was found to be 6.0 per cent., thus indicating a loss of total sodium due to hydrolysis and diffusion out of sodium hydroxide. In order to obtain a more marked difference, a diluted solution of the muddy-brown liquid obtained after three weeks' dialysis was subjected to further dialysis with daily renewal of the external water. After seven weeks' dialysis the muddy solution in the dialyser had assumed a violet hue, and the dried residue was now found to contain only 1.6 per cent. of sodium. A portion of this solution, still further diluted, on boiling in a glass beaker for some time became clear and bright red, being converted into a solution of the normal Congo-red salt by the alkali taken up from the glass. The above dialysed solution (total concentration about 0.15 gram per 100 c.c., sodium content of dry residue = 1.6 per cent.) gave in an osmometer an osmotic pressure of 40 mm. of water, that is, about 3 mm. of mercury, the measurement being made by substituting a vertical glass tube of narrow bore for the mercury manometer. This result appears to indicate that the first product of the hydrolysis of Congo-red must be mainly a "colloidal" suspension of the sodium hydrogen salt, since, if the free acid were in suspen-

sion, the solution which still contains 1.6 per cent. of sodium in its solid residue ought to have shown a much higher osmotic pressure than that observed.

A similar experiment with Kahlbaum's benzopurpurine-4B yielded the following results:

Initial sodium content of Kahlbaum's preparation	= 22.45 per cent. Na.
Sodium content of dried residue after six days' dialysis	= 6.0 per cent. Na.
Sodium content of dried residue after five weeks' dialysis	= 3.3 per cent. Na.*
Theoretical value for benzopurpurine	= 6.3 per cent. Na.

\* The solution in the osmometer after five weeks' dialysis contained approximately 1 gram per 100 c.c.

These results show that benzopurpurine suffers a much more rapid membrane-hydrolysis than Congo-red. This accounts for the fact that Biltz and von Vegesack found a solution of benzopurpurine (of initial concentration 1 per cent.) after three weeks' dialysis to show only a small osmotic pressure. The following experiment confirms this conclusion. A solution of benzopurpurine gave an osmotic pressure of 67.5 mm. of mercury, which fell to 6 mm. in fourteen days (final concentration about 0.25 per cent.), whilst with a Congo-red solution of final concentration 0.17 per cent. the pressure fell from 48 mm. to 34 mm. in nineteen days.

#### *Second Series of Osmotic Pressure Measurements.*

In the previous experiments the maximum pressures observed corresponded with solutions which had suffered some degree of hydrolysis, and were in consequence muddy-brown in appearance. In order to see whether this hydrolysis had sensibly vitiated the results, a series of experiments with solutions of the same initial concentrations of Grübler's Congo-red was carried out as follows. After the preliminary dialysis in the osmometer against pure water to remove the sodium chloride, a dilute solution of sodium hydroxide\* was used as external liquid in order to throw back the hydrolysis. This solution was then replaced by a more dilute solution of alkali, and so on, pure water being finally employed. In this way one may hope to obtain the maximum osmotic pressure against pure water without sensible disturbance, due either to hydrolysis or to presence of foreign electrolytes. The results are shown in the following table:

\* Prepared from metal and pure water free from carbonic acid.

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Room temperature 17°.

initial concentration (gram per 100 c.c.) (Congo-red + NaCl) .....	Osmom. I. mm. Hg.	Osmom. II. mm. Hg.	Osmom. III. mm. Hg.
.....	0.5	0.75	1.00
Max. reading after removal of NaCl .....	82.0	132.0	166.5
Reading after 24 hours with <i>N</i> /500-NaOH .....	52.0	90.0	132.0
" " " " <i>N</i> /1000-NaOH .....	57.0	104.0	143.0
" " " " <i>N</i> /2000-NaOH .....	68.0	117.0	153.0
" " " " <i>N</i> /4000-NaOH .....	79.0	128.0	165.0
" " " " <i>N</i> /8000-NaOH .....	81.0	131.0	167.0
" " " " <i>N</i> /16,000-NaOH .....	84.0	137.0	169.0
" " " " pure water .....	86.0	137.5	171.0
Correction for difference of levels .....	+ 3.0	+ 7.5	+ 0.7
Final osmotic pressure .....	89.0	145.0	171.7
Final concentration (gram per 100 c.c.) .....	0.357	0.564	0.700
"Calculated value" of osmotic pressure .....	92.7	148.4	179.0
Observed as percentage of calculated value .....	96.0%	99.0%	96.5%

These results satisfactorily substantiate those previously obtained, and show that at these concentrations and temperatures the osmotic pressure of a pure non-hydrolysed Congo-red solution approaches closely to that calculated for single undissociated molecules.

Third Series of Osmotic Pressure Measurements.

In these experiments, which were carried out according to Bayliss' method for the sake of comparison, the osmometer contained initially a solution (that is, colloidal solution) of pure Congo-red acid (prepared by dialysis of a mixture of Congo-red and hydrochloric acid). In the first experiment *N*/175-sodium hydroxide solution was employed initially as external liquid, in order to convert the Congo-red acid in the osmometer into the Congo-red (sodium) salt. After ten days this was replaced by *N*/1000-sodium hydroxide, which solution was replaced by *N*/2000-sodium hydroxide after twenty-four hours. The alkali solution was then regularly replaced by a more dilute one every twenty-four hours, and finally by pure water. The volume of outer liquid was 1 litre, as in the previous experiments, the temperature 17°. The following table shows the result of one experiment:

Concentration of alkali.	Difference of mercury levels.	Concentration of alkali.	Difference of mercury levels.
<i>N</i> /175	31.0 mm.	<i>N</i> /8000	116.5 mm.
<i>N</i> /1000	76.0 "	<i>N</i> /16,000	122.0 "
<i>N</i> /2000	98.0 "	<i>N</i> /32,000	121.8 "
<i>N</i> /4000	113.0 "	Water	121.0 "

The correction for difference of water and mercury levels was -2 mm., so that the maximum osmotic pressure observed was

120 mm. The final concentration of Congo-red being 0.491 gram per 100 c.c., the calculated value=124 mm. Hence, observed value=97 per cent. of calculated value.

Two other similar experiments gave the following final results:

Final conc. of Congo-red.	Observed pressure.	Calculated value.	Percentage.
0.423 gram/100 c.c.	106.0 mm. Hg.	109.5 mm.	97.0
0.346     "	88.7     "	90.0     "	98.5

These results show a good general agreement with those obtained by the other method.

#### *Fourth Series of Osmotic Pressure Measurements.*

These experiments were made with much more concentrated solutions of Congo-red. No alkali was used in the outside water. The latter was changed daily until no more sodium chloride diffused out, this requiring four to five days in the relatively more dilute solutions, and about eight days in the more concentrated solutions. As in the first series of measurements, the pressure rose to a maximum, and then slowly decreased, this maximum being reached after the sodium chloride was all (or practically all) removed. The final results are shown in the following table:

Final concentration.	Max. pressure observed.	Calculated value.	Percentage.
1.276 per cent.	310 mm.	331.8 mm.	93.4
2.617     "	603     "	676.0     "	89.0
5.016     "	1139    "	1304.0    "	87.3
6.033     "	1863    "	1567.0    "	86.9

In the last experiment in this series the form of manometer described by Adie (*Trans.*, 1891, **59**, 234) was employed. These results point perhaps to an increasing "aggregation" of the Congo-red in the stronger solutions, the osmotic pressure per molecule of Congo-red decreasing with increase of concentration.

#### *Behaviour of Sodium Chloride and Sodium Hydroxide alone in the Osmometer.*

A detailed examination of this behaviour was made, the results of which need only be briefly referred to. With the sodium chloride solutions (5*N*, *N*/10, *N*/100, *N*/1000) the pressure developed initially falls rapidly at first, afterwards very slowly. This is due to the fact that even when the salt has practically all diffused out, the hydrostatic pressure so established only falls slowly, owing to the slow rate at which water flows through the parchment diaphragm under small differences of pressure. A rapid rise, followed by a rapid fall of pressure, was observed at each change of the external water. This effect is very different from the otherwise somewhat similar one observed in the case of Congo-red solutions

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which are being freed from sodium chloride by dialysis. In the present case the rapid rise and succeeding rapid fall of pressure are undoubtedly due to the temporary osmotic pressure caused by the salt still present in the osmometer. In the case of the Congo-red solutions referred to, the rise of pressure on change of the external water is followed by a slow fall of pressure, the latter being due, as shown above, to the progressive membrane-hydrolysis; whilst the rise is due to the removal of the counter-pressure caused by the greater concentration of the salt in the external water.

A concentrated solution of sodium hydroxide appears to pass through the membrane very rapidly, whilst weak solutions do so very much more slowly. The conclusion of Roaf (*loc. cit.*) that diffusible electrolytes do not show any temporary osmotic pressure effects with parchment membranes is therefore incorrect. The following tables will give some idea of the nature of the results observable with the osmometers used in this work.

5N-Sodium chloride.		N/10-Sodium chloride.	
Time from filling.	Pressure.	Time from filling.	Pressure.
7½ hours	169.0 mm.	18½ hours	56.7 mm.
*48 "	42.0 "	68 "	24.0 "
53 "	54.5 "	*116 "	17.0 "
*4 days	33.5 "	140 "	26.0 "
4 " 8 hours	35.0 "	*188 "	20.0 "
5 "	27.5 "	194 "	19.5 "
*6 "	20.0 "		
6 " 8 hours	20.0 "		
7 "	18.0 "		
10 "	11.0 "		
N/2-Sodium hydroxide.		N/1000-Sodium hydroxide.	
0 hour	25.5 mm.	0 hours	23.0 mm.
*18 hours	2.5 "	3 "	36.0 "
49 "	36.4 "	*22 "	24.0 "
*90 "	29.0 "	28 "	21.0 "
95 "	35.4 "	70 "	14.5 "
*118 "	26.5 "	119 "	9.9 "
124 "	26.0 "		
160 "	17.0 "		

Indicates change of outside liquid.

## Electrical Conductivity of Congo-red Solutions.

In order to prepare Congo-red solutions for measurements of electrical conductivity, it was necessary to free them as far as possible from sodium chloride by dialysis, and at the same time to avoid any appreciable hydrolysis. For this purpose the hot saturated solution of Congo-red was placed in an osmometer vessel, the side-tube of which was closed by a rubber-tube and screw-clip. The osmometer vessel was then immersed in distilled water, free from carbon dioxide, which was changed daily for nineteen days.

By thus dialysing strong solutions at room temperature, and preventing dilution of the solutions during dialysis caused by osmotic flowing in of water, any appreciable hydrolysis was prevented, as it was found that hydrolysis increased the more dilute the solutions were. The contents of the osmometer at the end of the dialysis were diluted with "conductivity" water until the solid which had separated in the osmometer on cooling was all dissolved. Small portions of this solution, when diluted further with water, showed a clear red colour, indicating the absence of any appreciable hydrolysis.

The following table shows the results of the first series of measurements (temp. 25°). The more dilute solutions were obtained by diluting the dialysed solution with conductivity water.

Concentration of Congo-red.		Specific conductivity.	Molar conductivity.
Grams/100 c.c.	Mols./litre.		
2.667	1/26.1	$4.161 \times 10^{-3}$	108.5
1.333	1/52.2	$2.234 \times 10^{-3}$	119.2
0.667	1/104.4	$1.249 \times 10^{-3}$	130.4
0.333	1/208.8	$0.700 \times 10^{-3}$	146.2
0.1667	1/417.6	$0.390 \times 10^{-3}$	163.1
0.0833	1/835.2	$0.210 \times 10^{-3}$	175.7
0.0417	1/1670.4	$0.110 \times 10^{-3}$	183.5
	N/50-NaCl	$2.328 \times 10^{-3}$	116.4

For comparison are given the specific and molar conductivities of a N/50-sodium chloride solution at the same temperature. A portion of the strongest of the above dialysed solutions of Congo-red was evaporated to dryness, and the chlorine content of the dried residue determined. The analysis showed that the solution was not quite free from sodium chloride, containing 0.005 gram per 100 c.c. (that is, N/1170 with respect to sodium chloride).

A second solution of Congo-red was therefore dialysed in a similar manner for fourteen days, but in order to hasten the removal of the sodium chloride, a small air-space was left in the osmometer vessel, thus permitting the contents of the latter to be mixed by shaking. In this case the solution of Congo-red so obtained was found to be practically free from sodium chloride. Conductivity measurements with solutions prepared from this solution by dilution with conductivity water gave the following results (25°):

Concentration of Congo-red.		Specific conductivity.	Molar conductivity.
Grams/100 c.c.	Mols./litre.		
2.485	1/28	$3.664 \times 10^{-3}$	162.6
1.2425	1/56	$2.046 \times 10^{-3}$	114.6
0.6212	1/112	$1.125 \times 10^{-3}$	126.0
0.3106	1/224	$0.626 \times 10^{-3}$	140.2
0.1553	1/448	$0.352 \times 10^{-3}$	157.7
0.0776	1/896	$0.189 \times 10^{-3}$	169.3
0.0388	1/1792	$0.102 \times 10^{-3}$	182.8
	N/50-NaCl	$2.328 \times 10^{-3}$	116.4

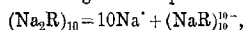
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As a further check, two measurements of osmotic pressure were made at room temperature (17°) with the dialysed solution used in the above conductivity measurements. The results may be briefly stated as follows:

Experiment 1:—Final concentration of solution	=	0.572 gram per 100 c.c.
Maximum pressure (reached in 4 days)	=	140.0 mm. Hg
Calculated value	=	148.7 " "
Observed value as percentage of calculated value	=	94
Experiment 2:—Final concentration of solution	=	0.257 gram per 100 c.c.
Maximum pressure (reached in 3 days)	=	62.5 mm. Hg.
Calculated value	=	66.7 " "
Observed value as percentage of calculated value	=	94

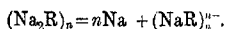
The conductivity-measurements show that Congo-red in aqueous solution behaves as a highly dissociated salt, although the observed value of the osmotic pressure indicates apparently no ionisation. At first sight one would be inclined to explain this somewhat anomalous result by the assumption of simultaneous "aggregation" and ionisation of the aggregated complex.

Consider, for example, a solution containing 1 gram of Congo-red in 100 c.c. The foregoing measurements show that at 17° the observed osmotic pressure of such a solution is somewhat less than 260 mm. (the value calculated for simple undissociated molecules). Suppose now that the solution contained only undissociated aggregates of the formula  $(\text{Na}_2\text{R})_{10}$ . This would lead to an osmotic pressure of only 26 mm. for the above-mentioned solution. If, however, we were to assume a complete "first stage" ionisation of these complexes according to the equation:



the osmotic pressure would be  $11 \times 26$ , or 286 mm.

In the same way the assumption of aggregates of the formula  $(\text{Na}_2\text{R})_{20}$  ionising in a similar manner would lead to an osmotic pressure of 273 mm. The assumption of the existence of such aggregates ionising (partially) in the manner indicated would therefore suffice to account for the osmotic pressures observed, and might perhaps serve to explain the non-diffusibility of Congo-red through parchment paper; but it is difficult to reconcile such an assumption with the high values obtained for the molar conductivities. Consider, for example, the 1/112-molar solution, the molar conductivity (referred to the formula  $\text{Na}_2\text{R}$ ) of which at 25° is 126. The observed osmotic pressure of this solution indicates a van't Hoff factor (referred to the formula  $\text{Na}_2\text{R}$ ) of practically unity. Let us suppose for a moment that this solution contained complexes of the (average) formula  $(\text{Na}_2\text{R})_n$ , very largely dissociated as indicated by the equation:



Then the molar conductivity referred to  $\text{Na}_2\text{R}$  would be approxi-



mately equal to the conductivity of 1 gram-molecule  $\text{Na}^+$ -ion plus  $1/n$ th the conductivity of 1 gram-molecule  $(\text{NaR})_n^{--}$ -ion. Now the latter term cannot exceed the conductivity of 1 gram-molecule  $(\text{NaR})^-$ -ion, which we may put at about 30–40 at  $25^\circ$ ; so that the molar conductivity of the solution cannot certainly exceed at  $25^\circ$   $50 + 40$ , that is, 90, whilst the observed value is 126. If therefore the observed conductivities correspond with solutions practically free from sodium chloride and not to any appreciable extent hydrolysed, it does not seem possible to reconcile them with any such explanation of the osmotic pressure results as that suggested above. On the other hand, the assumption that we are dealing with a simple salt  $\text{Na}_n\text{R}$ , dissociating into  $\text{Na}^+$ -ions and  $\text{R}_n^{--}$ -ions, although perhaps reconcilable with the measurements of conductivity, leads to degrees of dissociation and total molecular concentrations which are not in harmony with the observed values of the osmotic pressure. It must not be forgotten in this connexion that the value of the osmotic pressure (if it correspond with a true state of osmotic equilibrium) can be thermodynamically related to the vapour-pressure of the solution, which latter is a function of the total molecular concentration of the solution.

The explanation of this apparent contradiction probably lies in the fact that we are not dealing here with an ordinary case of osmotic equilibrium. The dissociated sodium ions can themselves rapidly pass through the parchment membrane, and are only prevented from doing so by the potential difference set up across the membrane.\* True equilibrium can only be attained, as shown in the present paper, when a certain concentration of  $\text{Na}^+$ - and  $(\text{OH})^-$ -ions is produced on the other side of the membrane. Under these conditions it is natural to expect that the  $\text{Na}^+$ -ions do not contribute in the ordinary way to the osmotic pressure.

*The Lowering of the Osmotic Pressure of Congo-red Solutions caused by Solutions of Sodium Chloride and Sodium Hydroxide.*

The experiments with pure sodium hydroxide (prepared from metal and water free from carbon dioxide) will first be described. In these experiments it was found that in presence of a definite concentration of sodium hydroxide, provided this concentration was not below a certain critical value, an absolutely constant osmotic pressure was obtained. Evidently in these cases the alkali concentration was sufficient to arrest the membrane-hydrolysis.†

\* These questions are fully dealt with in another paper.

† It will be shown in another paper that this experimental result is in full accord with the theory of the action of membranes in presence of electrolytes possessing a non-dialysing ion.

# CONDUCTIVITY OF AQUEOUS SOLUTIONS OF CONGO-RED. 1569

Below a certain concentration of alkali, the critical value being about  $N/1200$ -sodium hydroxide in the case of a 0.4 per cent. Congo-red solution, the pressure gradually decreased, and the previously clear red solution in the osmometer became muddy, showing that hydrolysis was occurring.

The procedure in the first experiment with sodium hydroxide was as follows. The osmometer was filled with a "solution" of Congo-red acid of concentration approximately the same as that used in the third series of experiments on osmotic pressure. This was converted completely into Congo-red salt by means of an  $N/90$ -solution of pure sodium hydroxide put outside the osmometer (all entrance of carbon dioxide was, of course, prevented as described previously), the volume of this solution being 1 litre. When the conversion was complete, the alkali solution was replaced by a litre of  $N/100$ -sodium hydroxide solution, when a constant pressure was attained after two to three days. The concentration of the alkali solution was then reduced to  $N/200$ , the pressure thereupon rising, and finally becoming quite constant after a few days. The alkali concentration was successively reduced in the way described, until finally pure water was used, which was changed from time to time until the maximum pressure was attained. The results of an experiment at  $25^\circ$  are shown below:

Concentration of alkali.	Osmotic pressure.
$N/100$	37.0 mm. Hg
$N/200$	57.7 " "
$N/400$	76.3 " "
$N/800$	96.0 " "
$N/1200$	104.6 " "
Pure water	114.5 " " (max. pressure).

In this experiment the final concentration of the Congo-red was 0.395 gram per 100 c.c., for which the calculated value of the osmotic pressure at  $25^\circ$  is 105.5 mm. The observed value in this case exceeds the "calculated value" by about 8 per cent. It is possible that this excess may be partly due to a little alkali still present inside the osmometer, as the maximum pressure was attained about six hours after the  $N/1200$ -solution had been replaced by pure water.

A second experiment was made at  $25^\circ$  under similar conditions, but after a constant pressure was obtained with  $N/800$ -sodium hydroxide solution, some sodium chloride was added to the outside liquid so as to make it  $N/800$ -sodium hydroxide +  $N/500$ -sodium chloride. The pressure decreased from the value obtained with  $N/800$ -sodium hydroxide alone, and again became constant. Constant pressures were similarly obtained with  $N/1600$ -sodium hydroxide +  $N/1000$ -sodium chloride, and with  $N/3200$ -sodium

hydroxide +  $N/2000$ -sodium chloride. After this the concentration of the mixed solution outside the osmometer was decreased daily until it reached the value  $N/25,600$ -sodium hydroxide +  $N/16,000$ -sodium chloride, when pure water, free from carbon dioxide, was substituted for it, the (final) concentration of the Congo-red solution in the osmometer being determined when the maximum pressure had been obtained and all sodium hydroxide and sodium chloride had been removed. The results of this second experiment are shown in the accompanying table (temperature  $25^{\circ}$ ).

Concentration.	Osmotic pressure. mm. Hg.	Concentration.	Osmotic pressure. mm. Hg.
$N/100$ -NaOH	33.0	$N/800$ -NaOH + $N/500$ -NaCl	61.0
$N/200$ -NaOH	53.0	$N/1600$ -NaOH + $N/1000$ -NaCl	79.0
$N/400$ -NaOH	73.0	$N/3200$ -NaOH + $N/2000$ -NaCl	91.0
$N/800$ -NaOH	93.0	Pure water (max. pressure)	107.0

In this experiment the concentration of the Congo-red solution was 0.383 gram per 100 c.c., for which the calculated value of the osmotic pressure at  $25^{\circ}$  is 102 mm. The observed (maximum) value is therefore about 5 per cent. higher than that calculated for simple undissociated molecules.

It may be remarked that a constant osmotic pressure (that is, absence of membrane-hydrolysis) is obtained with  $N/3200$ -sodium hydroxide +  $N/2000$ -sodium chloride, although hydrolysis occurs in presence of  $N/1600$ -sodium hydroxide alone, which shows that sodium chloride assists the sodium hydroxide in preventing hydrolysis, in spite of the fact (as will be shown presently) that even a fairly strong solution of sodium chloride alone cannot prevent hydrolysis occurring. It may also be remarked that the lowering effect of a mixture of sodium chloride and sodium hydroxide appears to be about the same as that of an equimolecular solution of pure sodium hydroxide. Thus  $N/800$ -sodium hydroxide +  $N/500$ -sodium chloride, which corresponds with a pressure of 61 mm., is approximately equimolecular with  $N/300$ -sodium hydroxide, for which the pressure has very nearly the same value, as may be seen by interpolation from the data given above.

The effect of sodium hydroxide on a more concentrated solution of Congo-red was next investigated. In this experiment the osmometer was filled with a strong solution of Grübler's Congo-red, as used in the fourth series of osmotic pressure measurements. A litre of distilled water, free from carbon dioxide, was placed outside the osmometer, and changed every day for fourteen days, when all the sodium chloride was removed and a maximum pressure of 722 mm. Hg developed. Up to this point the experiment was carried out at room temperature ( $17^{\circ}$ ). The pure water was now

replaced by a litre of *N*/25-sodium hydroxide, and the apparatus suspended in a thermostat at 25°. The pressure quickly dropped, becoming constant at 261 mm. in three days. As in the previous experiments, the constant pressures corresponding with more dilute solutions of sodium hydroxide were determined, and finally the alkali was replaced by pure water, which was changed daily until the maximum pressure was attained. The results are shown in the following table:

Concentration of sodium hydroxide.	Pressure.
<i>N</i> /25	261.0 mm.
<i>N</i> /50	405.0 "
<i>N</i> /100	551.0 "
<i>N</i> /200	636.0 "
<i>N</i> /400	687.0 "
Pure water (max. pressure)	763.6 "

The final concentration of the Congo-red was 3.10 grams per 10 c.c., for which the calculated value of the osmotic pressure at 10° is 828 mm., the observed value at 25° being thus 92 per cent. of the calculated value. The calculated value at 17° is 806 mm., the observed value (722 mm.) being in this case 89.6 per cent. of the calculated value. The osmotic pressure per molecule of the Congo-red solution appears therefore to increase more rapidly with increase of temperature than would correspond with the simple gas law. The effect of sodium chloride solutions alone on the osmotic pressure of Congo-red was next investigated. It was found, for example, that a normal solution of sodium chloride placed inside the osmometer was sufficient to reduce the osmotic pressure of a saturated solution of Grüber's Congo-red to zero. Under similar conditions a 0.5 per cent. solution of Grüber's Congo-red showed zero pressure, some of the Congo-red salt being precipitated in the osmometer. Another portion of this 0.5 per cent. solution contained in an osmometer immersed in *N*/25-sodium chloride solution showed a pressure of only 60 mm. of water (about 4.4 mm. Hg), no precipitation occurring in this case.

It was not possible to carry out exact measurements with sodium chloride as in the case of sodium hydroxide, for the pressures always fell slowly after attaining a maximum, owing to progressive hydrolysis.

The following is an example of many similar experiments. An osmometer was filled with a 2.5 per cent. solution of Grüber's Congo-red, and immersed in a litre of pure water, free from carbon dioxide, at room temperature (17°). The greater portion of the sodium chloride was removed by dialysis, which was continued for two days, with three changes of water. The pressure at this point having risen to 203 mm., the outside water was replaced by a

*N*/25-sodium chloride solution, the pressure immediately falling and becoming fairly steady at 82 mm. in three to four days. The concentration of the outside sodium chloride solution was then successively reduced, and the approximately steady values of the pressure noted. Finally, pure water was used, and changed daily until all salt was dialysed out and the maximum pressure obtained. The results are given below (temperature 17°).

Concentration of sodium chloride.	Pressure.
<i>N</i> /25	82 mm.
<i>N</i> /50	131 "
<i>N</i> /100	191 "
<i>N</i> /200	259 "
Pure water (max. pressure)	365 "

This solution contained 1.713 grams of Congo-red per 100 c.c. for which the calculated value of the pressure at 17° is 446 mm. The observed maximum pressure is only 82 per cent. of this, which is to be accounted for by hydrolysis occurring in the osmometer, the dialysis having lasted thirty-one days in all.

*Cause of the Lowering of Pressure produced by Sodium Chloride and Sodium Hydroxide.*

If the remarkable effects produced by sodium chloride and sodium hydroxide on the osmotic pressure of a Congo-red solution were due solely, as Bayliss supposes, to an increased aggregation of the Congo-red, we might expect this to show itself in a greatly reduced conductivity. Experiment shows, however, that on mixing a solution of pure Congo-red with enough sodium chloride solution to effect an enormous lowering in the measured osmotic pressure, the conductivity of the mixed solution only shows the usual small deviation from the additive law to be expected in a mixture of two strong electrolytes which slightly influence each other's dissociation. The following data illustrate this, the values given being the conductances (not the specific conductivities), as measured in a certain conductivity cell at 25° (in reciprocal ohms).

Concentration of Congo-red solution = 2.485 per cent.	
10 c.c. of Congo-red solution + 10 c.c. of conductivity water .....	$2.651 \times 10^{-2}$
10 c.c. of <i>N</i> /50-sodium chloride + 10 c.c. of conductivity water .....	$1.565 \times 10^{-2}$
10 c.c. of Congo-red solution + 10 c.c. of <i>N</i> /50-sodium chloride .....	$3.940 \times 10^{-2}$

It will be seen that the last value is only slightly less than the sum of the two others. From the table given above it will also be seen that a *N*/50-sodium chloride solution lowers the osmotic pressure of a Congo-red solution (containing 1.7 grams of Congo-red per 100 c.c.) from 365 mm. to 131 mm.

Before discussing another possible explanation of the effects produced by sodium chloride and sodium hydroxide on the osmotic

pressure, an account will be given of experiments which have revealed a new and hitherto quite unsuspected phenomenon. It will be shown that when Congo-red is present on one side of a parchment diaphragm, sodium chloride (that is, total  $\text{Cl}^-$ -ion) does not distribute itself in equal concentration on both sides, although the membrane of parchment paper is perfectly permeable to both  $\text{Na}^+$  and  $\text{Cl}^-$ .

In the first experiment, 5 grams of Merck's Congo-red dissolved in 200 c.c. of distilled water, free from carbon dioxide, were placed inside a parchment dialysing tube suspended in a large beaker containing a litre of pure distilled water. By means of three changes of water the greater portion of the admixed salts was removed, the dialysis being continued for twenty-four hours. Then the outer water was replaced by a litre of  $N/10$ -sodium chloride solution. After thirteen days the chlorine content of the inside and outside liquids was determined. This was done by withdrawing 50 c.c. of each by means of a pipette, evaporating to dryness, heating the residues over a Bunsen flame for about a quarter of an hour (by which procedure the Congo-red from the inner liquid was charred, the residue from the outer liquid being subjected to the same process so as to have similar conditions), extracting with hot water, and estimating as silver chloride by precipitation in the usual way. The results were as follows:

*Outer liquid:* 5.106 grams of sodium chloride per litre.

*Inner liquid:* 4.478 " " " " "

The concentration of the Congo-red in the inner solution was determined, and found to be 1.074 per cent. At the same time the conductances of a given cell (at  $25^\circ$ ) filled with each of the two solutions were determined, with the following results:

Liquid used.	Conductance of cell (in mhos).
Inner	$12.99 \times 10^{-2}$
Outer	$12.50 \times 10^{-2}$

The foregoing experiment shows that after thirteen days' dialysis the concentration of the sodium chloride in the outer solution is undoubtedly greater than that in the inner solution containing the Congo-red. In order to obviate the natural objection that in the above experiment the sodium chloride might have been still diffusing into the inner solution, two further experiments were made, in which the concentration of the sodium chloride was initially higher in the inner solution (containing the Congo-red). In the first experiment, a mixture of approximately 2.8 grams of pure Congo-red and 7.2 grams of sodium chloride dissolved in 200 c.c. of conductivity water was placed inside the dialyser and a litre of pure water outside. After six days' dialysis the inner

liquid contained 5.136 grams of sodium chloride per litre, and the outer liquid 5.728 grams. The concentration of Congo-red in the inner liquid was 0.917 gram per 100 c.c.

In the next experiment the inner solution consisted initially of about 2.1 grams of pure Congo-red and 3.9 grams of sodium chloride, dissolved in 200 c.c. of pure water, the outer liquid being, as before, a litre of pure water. After five days' dialysis the inner liquid contained 2.53 grams of sodium chloride per litre, and the outer liquid 3.03 grams. The concentration of Congo-red in the inner liquid was 0.875 gram per 100 c.c.

These results show that we are dealing with a reversible equilibrium, and that the equilibrium state corresponds with a greater concentration of sodium chloride on the opposite side of the membrane to the Congo-red. Now this unequal distribution will clearly set up, in the osmotic pressure experiments, a counter osmotic pressure, which will make the observed osmotic pressure lower than that corresponding with the Congo-red.

The following calculation will serve to indicate the amount of this counter pressure. Consider the first of the three experiments given above. The osmotic pressure (at 0°) of the outer solution of sodium chloride will be  $22.4 \times 760 \times \frac{5.106}{58.5} \times i_1$  mm. Hg, where  $i_1$  = van't Hoff's factor for a solution of this concentration. The osmotic pressure due to the sodium chloride concentration in the inner solution will be similarly  $22.4 \times 760 \times \frac{4.478}{58.5} \times i_2$ . Putting  $i_1 = i_2 = 1.85$ , we get for the counter osmotic pressure at 17° (in mm. Hg):

$$22.4 \times 760 \times \frac{290}{273} \times \frac{0.628}{58.5} \times 1.85,$$

or 359 mm. Now the osmotic pressure at 17° of the Congo-red solution present in this experiment (containing 1.074 per cent. of Congo-red) would, according to the data given previously, amount to about 290 mm. Hence the approximately  $N/12$  solution of sodium chloride of this experiment would more than suffice to annul the osmotic pressure of the 1.074 per cent. Congo-red solution.

These considerations show that the unequal concentrations of an electrolyte (such as sodium chloride) with a common ion, which exist at equilibrium on either side of the membrane in presence of Congo-red on one side only, are sufficient to explain the apparent lowering effect of these electrolytes on the osmotic pressure of a solution of Congo-red. The results obtained by Bayliss with Congo-red and by Biltz and Vegesack with benzopurpurine are now intelligible, without any special assumptions as to the effect of the

electrolytes on the aggregation of the molecules of the electrolytic colloid. It is, of course, possible that some such aggregation may occur, but the results of the present paper show that the unequal distribution discovered in the present work is a sufficient explanation.

This unequal distribution can be easily shown to be thermodynamically necessary.\* Suppose we have on one side of a membrane a solution of the salt NaX, the membrane being supposed permeable to Na<sup>+</sup>, but impermeable to X<sup>-</sup> and to undissociated NaX. Let now a solution of sodium chloride be put on the other side of the membrane, the latter being supposed permeable to Cl<sup>-</sup> and sodium chloride. The initial state can be represented as follows:



Na<sup>+</sup>- and Cl<sup>-</sup>-ions will now begin to diffuse from (2) to (1). Equilibrium will be attained when the work gained by the isothermal reversible transport of  $\delta n$  gram-mol. Cl<sup>-</sup>-ion from (2) to (1) is equal to the work required for the isothermal reversible transport of  $\delta n$  gram-mol. Na<sup>+</sup>-ion from (2) to (1), that is:

$$\delta n \cdot RT \log \frac{[\text{Na}^+]_1}{[\text{Na}^+]_2} = \delta n \cdot RT \log \frac{[\text{Cl}^-]_2}{[\text{Cl}^-]_1},$$

where the square brackets indicate molar concentrations at equilibrium.

Hence:

$$\frac{[\text{Na}^+]_1}{[\text{Na}^+]_2} = \frac{[\text{Cl}^-]_2}{[\text{Cl}^-]_1}.$$

Now since at equilibrium we have in (1) both NaX and sodium chloride, in general  $[\text{Na}^+]_1 > [\text{Cl}^-]_1$ . Also from the above  $[\text{Cl}^-]_2 = [\text{Na}^+]_1 \times [\text{Cl}^-]_1$ . Hence  $[\text{Cl}^-]_2 > [\text{Cl}^-]_1$ . For highly dissociated solutions we shall therefore find the total "chlorine" concentration in (2) greater than that in (1). This has actually been shown to be the case in the experiments described in this paper.

Since the conclusion of this work a further paper has been published by Biltz and von Vegesack (*Zeitsch. physikal. Chem.*, 1910, **73**, 481), in which, contrary to their previous work, they find that both benzopurpurine and Congo-red exhibit considerable osmotic pressures. From measurements made in presence of other electrolytes they obtain values for the osmotic pressure which lead them to the conclusion that the true value for the molecular weight of Congo-red in aqueous solution is in the neighbourhood of 2000. It may be pointed out, however, that this conclusion is not binding,

\* In a paper which is ready for publication, the thermodynamical theory of such "membrane equilibria" will be more fully considered.



for, as shown in the present paper, the other electrolytes present will be unequally distributed on either side of the membrane, and so give rise to a counter osmotic pressure. The experimentally observed pressure will therefore be lower, and the value calculated for the molecular weight higher, than that which would be obtained if no foreign electrolytes were present.

#### *Summary of Results.*

(1) It has been shown that Congo-red gives against pure water an osmotic pressure agreeing approximately with that which would be obtained if it existed in aqueous solution as single undissociated molecules. The values found agree as to order of magnitude with those recorded by Bayliss (*loc. cit.*).

(2) Conductivity measurements show that Congo-red is a highly dissociated electrolyte.

(3) From the results of the conductivity measurements it is concluded that Congo-red exists in aqueous solution very largely as a simple and considerably dissociated salt.

(4) On dialysis, both Congo-red and benzopurpurine-4B undergo a peculiar "membrane-hydrolysis," sodium ions in company with hydroxyl ions diffusing out, and the free acids, acid salts, or some other insoluble phase being gradually aggregated or thrown out of solution inside the dialyser or osmometer. This "membrane-hydrolysis" can be prevented by solutions of alkali hydroxide above a certain definite concentration, the latter varying with the temperature and the concentration of the dye-salt. The gradual fall of osmotic pressure observed with pure water as external liquid is due to the membrane-hydrolysis.

(5) A consideration of the results given under (1) to (4) show that the osmotic pressures observed do not correspond with an ordinary state of osmotic equilibrium, inasmuch as the otherwise diffusible sodium ions are arrested in their diffusion across the membrane by potential differences, and do actually pass slowly through, to a certain extent, in company with hydroxyl ions.

(6) The osmotic pressure of a solution of Congo-red is lowered by sodium hydroxide and sodium chloride, the fall of pressure increasing with the concentration of these electrolytes.

(7) Sodium chloride distributes itself in unequal concentrations on either side of the parchment paper membrane when Congo-red is present on one side. A reversible ionic equilibrium is produced, the concentration of the sodium chloride at equilibrium being higher on the side of the membrane opposite to that in which the Congo-red is present.

(8) This highly important and interesting "membrane-equili-

brium" has been shown to be thermodynamically necessary, and is part of a group of very general and important phenomena.

(9) The counter osmotic pressure caused by the unequal distribution of sodium chloride (or sodium hydroxide) referred to in (7) is probably to a very large extent sufficient to account for the effects described under (6).

(10) Measurements of the osmotic pressures exhibited by an electrolyte with a non-dialysable ion in presence of other electrolytes cannot be used to draw conclusions concerning the molecular state in solution of the former, unless account be taken of the unequal distribution referred to in (7) and (9).

THE MUSPRATT LABORATORY OF PHYSICAL AND  
ELECTRO-CHEMISTRY, UNIVERSITY OF LIVERPOOL.

# CLXXVIII.—*Synthesis of Polypeptides of $\alpha$ -Amino-n-nonoic Acid with Glycine, Alanine, Valine, Leucine, Asparagine, and Aspartic Acid.*

By ARTHUR HOPWOOD and CHARLES WEIZMANN.

As peptides of  $\alpha$ -amino-n-nonoic acid with glycine and other amino-acids probably occur in the degradation products of the proteins contained in beet root, the leaves of *Pelargonium roseum*, and other plants, the authors have prepared the dipeptides of  $\alpha$ -amino-n-nonoic acid with glycine, alanine, valine, leucine, asparagine, and aspartic acid, and, in addition, the tripeptide leucyl- $\alpha$ -amino-n-nonylglycine.

## EXPERIMENTAL.

The method of synthesis adopted was the same as that which the authors (this vol., p. 571) applied in the synthesis of dipeptides of  $\alpha$ -aminolauric acid with glycine and other amino-acids. Briefly, the method consists in condensing  $\alpha$ -bromo-n-nonyl chloride with the amino-acids in presence of sodium hydroxide, and then displacing the bromine in the product by an amino-group through the action of ammonia.

### $\alpha$ -Bromo-n-nonyl Chloride, $C_8H_{16}Br\cdot COCl$ .

One hundred and forty grams of phosphorus pentachloride are added gradually, with vigorous shaking, to 170 grams of  $\alpha$ -bromo-n-nonoic acid, and, after the energetic action has subsided, the

mixture is heated on a water-bath for an hour. The product is distilled under diminished pressure, and the fraction boiling at 100–120°/9 mm. is collected. Yield, 150 grams:

0.2570 gave  $\text{AgCl} + \text{AgBr} = 0.3341$ .  $\text{Cl} + \text{Br} = 45.28$ .

$\text{C}_9\text{H}_{16}\text{OClBr}$  requires  $\text{Cl} + \text{Br} = 45.17$  per cent.

*$\alpha$ -Bromo-n-nonyl chloride* is a colourless liquid, which boils at 108–110°/9 mm., and at 118–125°/15 mm. It has a pungent odour, and is decomposed slowly by water and fairly readily by alkalis.

*$\alpha$ -Bromo-n-nonylglycine*,  $\text{C}_8\text{H}_{16}\text{Br}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ .

Ten grams of  *$\alpha$ -bromo-n-nonyl chloride* (1 mol.) and 50 c.c. of *N*-sodium hydroxide (1.25 mol.) are added gradually and alternately, with frequent shaking, to a solution containing 2.9 grams of glycine (1 mol.) dissolved in 40 c.c. of *N*-sodium hydroxide (1 mol.). The solution is heated on a water-bath until the odour of  *$\alpha$ -bromo-n-nonyl chloride* disappears, then allowed to cool, and dilute hydrochloric acid added in slight excess. A colourless precipitate of impure  *$\alpha$ -bromo-n-nonylglycine* separates out, which is kept for several hours, then collected, washed with cold water, and dried in air on a porous plate. Yield, 9.1 grams. On crystallising the product from benzene, a mixture of colourless, rhombic plates and rhombic prisms is obtained, which melts at 115.5–117° to a colourless liquid. The crystals are sparingly soluble in cold, but fairly soluble in hot, water or benzene. They are readily soluble in alcohol, ether, or alkalis:

0.1520 gave 0.0959  $\text{AgBr}$ .  $\text{Br} = 26.85$ .

$\text{C}_{11}\text{H}_{20}\text{O}_3\text{NBr}$  requires  $\text{Br} = 27.17$  per cent.

*$\alpha$ -Amino-n-nonylglycine*,  $\text{NH}_2\cdot\text{C}_8\text{H}_{16}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ .

Five grams of  *$\alpha$ -bromo-n-nonylglycine* are mixed with excess of concentrated aqueous ammonia, and then heated at 100° for an hour in a pressure flask. The resulting solution is evaporated slowly on a water-bath until the excess of ammonia is removed. In order to remove the ammonium bromide and unchanged  *$\alpha$ -bromo-n-nonylglycine*, the dry residue is boiled with absolute alcohol, and then collected, when 3.5 grams of nearly pure  *$\alpha$ -amino-n-nonylglycine* are obtained. For further purification, the dipeptide is dissolved in absolute alcohol containing a little aqueous ammonia, the solution filtered, and the filtrate boiled until the ammonia disappears, when the pure peptide separates out, and is collected, washed with absolute alcohol, and dried in air on a porous plate. It forms a mixture of colourless, monoclinic needles and rhombic

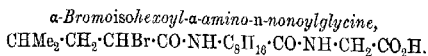
plates, which sinters at 205°, and melts and decomposes at 215—216°:

0.2462 gave 0.5160 CO<sub>2</sub> and 0.2143 H<sub>2</sub>O. C=57.15; H=9.74.

0.2937 „ 31.4 c.c. N<sub>2</sub> at 17.6° and 750 mm. N=12.40.

C<sub>11</sub>H<sub>20</sub>O<sub>3</sub>N<sub>2</sub> requires C=57.35; H=9.63; N=12.17 per cent.

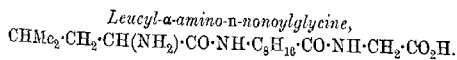
The dipeptide is fairly soluble in water, almost insoluble in alcohol or benzene, but readily soluble in ammonia, alkali hydroxides, or mineral acids. When dissolved in dilute sulphuric acid, it gives a white, amorphous precipitate with an aqueous solution of phosphotungstic acid, which, as in the case of the proteins, is soluble in excess of the reagent. In presence of sodium hydroxide, the dipeptide condenses with *β*-naphthalenesulphonyl chloride, yielding *β*-naphthalenesulphonyl-*α*-amino-*n*-nonoylglycine, which crystallises from water in colourless, rhombic prisms and rhombic plates, melting sluggishly at 203—206° to a viscid, yellow liquid, which darkens on further heating, and suddenly turns to a mobile, brown liquid at 213—215°.



One gram of *α*-amino-*n*-nonoylglycine (1 mol.) dissolved in 5.5 c.c. of *N*-sodium hydroxide (1.25 mol.), when treated with 1.23 grams of *α*-bromoisohexoyl bromide (1.1 mol.) and 6.5 c.c. of *N*-sodium hydroxide (1.5 mol.) in the same way as previously described for *α*-bromo-*n*-nonoylglycine, and afterwards acidified with hydrochloric acid, yields 2.0 grams of impure *α*-bromoisohexoyl-*α*-amino-*n*-nonoylglycine. The product crystallises from benzene or dilute alcohol as a mixture of colourless, prismatic needles and rhombic plates. When crystallised from benzene, the mixture of stereoisomerides melts sluggishly at 88—96°, yielding a colourless liquid, but when crystallised from dilute alcohol the mixture melts at 116—119°. The crystals are sparingly soluble in cold, but moderately so in hot, water. They are sparingly soluble in cold, but readily so in hot, benzene. They are also readily soluble in cold absolute alcohol, ether, ammonia, or alkali hydroxides:

0.1560 gave 0.0730 AgBr. Br=19.92.

C<sub>17</sub>H<sub>31</sub>O<sub>4</sub>N<sub>2</sub>Br requires Br=19.63 per cent.



One gram of *α*-bromoisohexoyl-*α*-amino-*n*-nonoylglycine, when treated with aqueous ammonia in the same way as described for *α*-bromo-*n*-nonoylglycine, yields 0.7 gram of *leucyl-α*-amino-*n*-nonoyl-

*glycine*, which crystallises from alcohol containing a little ammonia as a mixture of colourless, rhombic plates and small needles. When quickly heated, it sinters at 206°, and melts sluggishly with much decomposition at 214—222°. The tripeptide is almost insoluble in water, or dilute or absolute alcohol, but readily dissolves in ammonia, alkali hydroxides, or mineral acids. A white, amorphous precipitate is produced when an aqueous solution of phosphotungstic acid is added to a solution of the tripeptide in dilute sulphuric acid, the precipitate being soluble in excess of the reagent:

0.1006 gave 0.2190 CO<sub>2</sub> and 0.0880 H<sub>2</sub>O. C=59.36; H=9.79.

0.1019 „ 11.1 c.c. N<sub>2</sub> at 24.4° and 765.2 mm. N=12.59.

C<sub>17</sub>H<sub>35</sub>O<sub>4</sub>N<sub>3</sub> requires C=59.41; H=9.69; N=12.24 per cent.

*α-Bromo-n-nonoylalanine*, C<sub>8</sub>H<sub>16</sub>·Br·CO·NH·CHMe·CO<sub>2</sub>H.

3.5 Grams of alanine (1 mol.) dissolved in 40 c.c. of *N*-sodium hydroxide (1 mol.) treated in the same way as previously described for *α*-bromo-*n*-nonoylglycine with 10 grams of *α*-bromo-*n*-nonoyl chloride (1 mol.) and 40 c.c. of *N*-sodium hydroxide (1 mol.), and afterwards acidified with dilute hydrochloric acid, yield an oily precipitate of impure *α*-bromo-*n*-nonoylalanine. On prolonged keeping in an ice-chest, the oil slowly crystallises, and may then be collected, washed with water, and dried. The process may, however, be hastened considerably by extracting the oil with ether, evaporating off the latter at the ordinary temperature, placing the oily residue for a few hours in a vacuum desiccator, and then precipitating the *α*-bromo-*n*-nonoylalanine with light petroleum. Yield, 7.1 grams. The product crystallises from benzene in colourless, rhombic plates, which melt at 135.5—138°, yielding a colourless liquid. The crystals are sparingly soluble in cold, and moderately so in hot, water. They are only sparingly soluble in cold, but readily so in hot, benzene. They are also readily soluble in dilute or absolute alcohol, ether, ammonia, or alkali hydroxides:

0.1276 gave 0.0780 AgBr. Br=26.02.

C<sub>12</sub>H<sub>22</sub>O<sub>3</sub>NBr requires Br=25.93 per cent.

*α-Amino-n-nonoylalanine*, NH<sub>2</sub>·C<sub>8</sub>H<sub>16</sub>·CO·NH·CHMe·CO<sub>2</sub>H.

Five grams of *α*-bromo-*n*-nonoylalanine, when treated with aqueous ammonia in the same way as described for *α*-bromo-*n*-nonoylglycine, yield 3.0 grams of *α*-amino-*n*-nonoylalanine, which crystallises from alcohol in colourless prisms, melting and decomposing at 209—214°. The dipeptide is sparingly soluble in water, moderately so in dilute or absolute alcohol, and readily so in ammonia, alkali hydroxides, or mineral acids. When dissolved in dilute sulphuric acid it gives

a white, amorphous precipitate with an aqueous solution of phosphotungstic acid, which is soluble in excess of the reagent:

0.2033 gave 0.4384  $\text{CO}_2$  and 0.1756  $\text{H}_2\text{O}$ .  $\text{C}=58.82$ ;  $\text{H}=9.67$ .

0.1892 „ 18.8 c.c.  $\text{N}_2$  at  $19^\circ$  and 769.4 mm.  $\text{N}=11.76$ .

$\text{C}_{12}\text{H}_{24}\text{O}_3\text{N}_2$  requires  $\text{C}=58.96$ ;  $\text{H}=9.90$ ;  $\text{N}=11.48$  per cent.

$\alpha$ -Bromo-*n*-nonoylvaline,  $\text{C}_8\text{H}_{16}\text{Br}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CHMe}_2$ .

4.6 Grams of valine (1 mol.) dissolved in 50 c.c. of *N*-sodium hydroxide (1.25 mol.) treated with 10 grams of  $\alpha$ -bromo-*n*-nonoyl chloride (1 mol.) and 50 c.c. of *N*-sodium hydroxide (1.25 mol.) in the same way as previously described for  $\alpha$ -bromo-*n*-nonoylglycine, and afterwards acidified with hydrochloric acid, yield 12.0 grams of impure  $\alpha$ -bromo-*n*-nonoylvaline. The product crystallises from benzene in hexagonal plates, and from dilute alcohol in rhombic plates, which melt at  $156$ – $159^\circ$  to a colourless liquid. The crystals are sparingly soluble in hot, but practically insoluble in cold, water. They are fairly soluble in dilute alcohol, moderately so in hot benzene, and readily so in absolute alcohol, ether, ammonia, or alkalis:

0.1669 gave 0.0936  $\text{AgBr}$ .  $\text{Br}=23.87$ .

$\text{C}_{14}\text{H}_{26}\text{O}_3\text{NBr}$  requires  $\text{Br}=23.78$  per cent.

$\alpha$ -Amino-*n*-nonoylvaline,  $\text{NH}_2\cdot\text{C}_8\text{H}_{16}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CHMe}_2$ .

Five grams of  $\alpha$ -bromo-*n*-nonoylvaline, when treated with aqueous ammonia in the same way as described for  $\alpha$ -bromo-*n*-nonoylglycine, yield 3.5 grams of  $\alpha$ -amino-*n*-nonoylvaline, which crystallises from alcohol in rhombic plates, sintering at  $208^\circ$ , and melting and decomposing at  $223$ – $225^\circ$ . The dipeptide is sparingly soluble in water or alcohol, but readily so in ammonia, alkali hydroxides, or mineral acids. A white, amorphous precipitate is produced when an aqueous solution of phosphotungstic acid is added to a solution of the dipeptide in dilute sulphuric acid, the precipitate being soluble in excess of the reagent:

0.1305 gave 0.2726  $\text{CO}_2$  and 0.1108  $\text{H}_2\text{O}$ .  $\text{C}=61.69$ ;  $\text{H}=10.29$ .

0.2992 „ 26.8 c.c.  $\text{N}_2$  at  $21.8^\circ$  and 772 mm.  $\text{N}=10.54$ .

$\text{C}_{14}\text{H}_{28}\text{O}_3\text{N}_2$  requires  $\text{C}=61.70$ ;  $\text{H}=10.36$ ;  $\text{N}=10.29$  per cent.

$\alpha$ -Bromoisovaleryl- $\alpha$ -amino-*n*-nonoylvaline,  
 $\text{CHMe}_2\cdot\text{CHBr}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_8\text{H}_{16}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CHMe}_2$ .

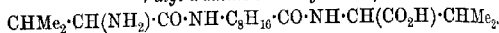
One gram of  $\alpha$ -amino-*n*-nonoylvaline (1 mol.) dissolved in 4.6 c.c. of *N*-sodium hydroxide (1.25 mol.) treated in the same way as previously described for  $\alpha$ -bromo-*n*-nonoylglycine with 1.0 gram of  $\alpha$ -bromoisovaleryl bromide (1.1 mol.) and 5.5 c.c. of *N*-sodium

hydroxide (1.5 mol.), and afterwards acidified with hydrochloric acid, yields 2 grams of impure  $\alpha$ -bromoisovaleryl- $\alpha$ -amino-*n*-nonoylvaline. The product crystallises from benzene in stout, prismatic needles, which melt at 179—181° to a colourless liquid. The crystals are sparingly soluble in hot, and almost insoluble in cold, water. They are only sparingly soluble in cold, but readily so in hot, benzene. They are also readily soluble in absolute alcohol, ether, ammonia, and alkalis:

0.1172 gave 0.0509 AgBr. Br=18.48.

$C_{18}H_{35}O_4N_2Br$  requires Br=18.36 per cent.

*Valyl- $\alpha$ -amino-*n*-nonoylvaline,*



The conversion of  $\alpha$ -bromoisovaleryl- $\alpha$ -amino-*n*-nonoylvaline into valyl- $\alpha$ -amino-*n*-nonoylvaline by aqueous ammonia is attended with considerable difficulty. On treating the bromo-compound with concentrated aqueous ammonia, either in the cold for days or at 100° for four hours, practically no change takes place. The stability of  $\alpha$ -bromoisovaleryl derivatives towards aqueous ammonia appears to be general, as Fischer and Schenkel (*Annalen*, 1907, 354, 12—20) had similar difficulties with  $\alpha$ -bromoisovalerylglycine and  $\alpha$ -bromoisovalerylalanine.

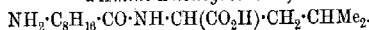
*$\alpha$ -Bromo-*n*-nonoyl-leucine,*  $C_8H_{16}Br \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2 \cdot CHMe_2$ .

Five grams of *r*-leucine (1 mol.) dissolved in 40 c.c. of *N*-sodium hydroxide (1 mol.) when treated in the same way as described for  $\alpha$ -bromo-*n*-nonoylglycine with 10 grams of  $\alpha$ -bromo-*n*-nonoyl chloride (1 mol.) and 50 c.c. of *N*-sodium hydroxide (1.25 mol.), and afterwards acidified with hydrochloric acid, yield 11 grams of impure  $\alpha$ -bromo-*n*-nonoyl-leucine. The product crystallises from benzene as a mixture of colourless, rhombic plates and prismatic needles, which melts at 130—132.5° to a colourless liquid. The crystals are sparingly soluble in hot, but almost insoluble in cold, water. They are readily soluble in hot, but sparingly so in cold, benzene. They are also readily soluble in cold absolute alcohol, ether, ammonia, or alkalis:

0.2198 gave 0.1173 AgBr. Br=22.72.

$C_{15}H_{28}O_3NBr$  requires Br=22.82 per cent.

*$\alpha$ -Amino-*n*-nonoyl-leucine,*



Two grams of  $\alpha$ -bromo-*n*-nonoyl-leucine, when treated with aqueous ammonia in the same way as described for  $\alpha$ -bromo-

$\alpha$ -AMINO-NONANOIC ACID WITH GLYCINE, ALANINE, ETC. 1583

*n*-nonoylglycine, yield 1.5 grams of  $\alpha$ -amino-*n*-nonoyl-leucine, which crystallises from alcohol in small, prismatic needles, mixed with a few rhombic plates. When heated rapidly, it softens at  $234^{\circ}$ , and melts and decomposes at  $237$ – $238^{\circ}$ . The dipeptide is sparingly soluble in water, moderately so in dilute or absolute alcohol, and readily so in ammonia, alkali hydroxides, or mineral acids. When dissolved in dilute sulphuric acid, it yields a white, amorphous precipitate with an aqueous solution of phosphotungstic acid, which is soluble in excess of the reagent:

0.1612 gave 0.3709  $\text{CO}_2$  and 0.1569  $\text{H}_2\text{O}$ .  $\text{C}=62.75$ ;  $\text{H}=10.56$ ;

0.1186 " 9.8 c.c.  $\text{N}_2$  at  $22.2^{\circ}$  and 773.5 mm.  $\text{N}=9.79$  per cent.

$\text{C}_{15}\text{H}_{29}\text{O}_3\text{N}_2$  requires  $\text{C}=62.87$ ;  $\text{H}=10.56$ ;  $\text{N}=9.79$  per cent.

$\alpha$ -Bromo-*n*-nonoylasparagine,  
 $\text{C}_8\text{H}_{16}\text{Br}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ .

5.9 Grams of *L*-asparagine (1 mol.) dissolved in 10 c.c. of *N*-sodium hydroxide (1 mol.) treated in the cold as described for  $\alpha$ -bromo-*n*-nonoylglycine with 10 grams of  $\alpha$ -bromo-*n*-nonoyl chloride (1 mol.) and 40 c.c. of *N*-sodium hydroxide (1 mol.), and after neutralising with dilute hydrochloric acid, yield 14.0 grams of  $\alpha$ -bromo-*n*-nonoylasparagine. The product crystallises from absolute alcohol in rhombic prisms, which melt and decompose at  $163$ – $164^{\circ}$ . The crystals are moderately soluble in hot, but sparingly so in cold water. They are only moderately soluble in cold, but readily soluble in hot, dilute or absolute alcohol. They are also readily soluble in cold ammonia or alkalis, but are insoluble in ether or benzene:

0.1486 gave 0.0801  $\text{AgBr}$ .  $\text{Br}=22.94$ .

$\text{C}_{15}\text{H}_{29}\text{O}_4\text{N}_2\text{Br}$  requires  $\text{Br}=22.76$  per cent.

$\alpha$ -Amino-*n*-nonoylasparagine,  
 $\text{NH}_2\cdot\text{C}_8\text{H}_{16}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ .

One gram of  $\alpha$ -bromo-*n*-nonoylasparagine, when treated with aqueous ammonia in the same way as described for  $\alpha$ -bromo-*n*-nonoylglycine, yields 0.5 gram of  $\alpha$ -amino-*n*-nonoylasparagine, which crystallises from absolute alcohol containing a few drops of ammonia in fine needles. It sinters at  $236^{\circ}$  and melts sluggishly, and decomposes at  $251$ – $256^{\circ}$ . The dipeptide is only sparingly soluble in water or alcohol, but readily so in ammonia, alkali hydroxides, or mineral acids. When dissolved in dilute sulphuric acid, it yields a white, amorphous precipitate with an aqueous solution of phosphotungstic acid, which is soluble in excess of the reagent:



0.1670 gave 0.3316  $\text{CO}_2$  and 0.1328  $\text{H}_2\text{O}$ .  $\text{C}=54.16$ ;  $\text{H}=8.90$ .

0.2544 „ 32.0 c.c.  $\text{N}_2$  at 22.7 and 756.9 mm.  $\text{N}=14.46$ .

$\text{C}_{13}\text{H}_{25}\text{O}_4\text{N}_3$  requires  $\text{C}=54.30$ ;  $\text{H}=8.77$ ;  $\text{N}=14.63$  per cent.

*$\alpha$ -Bromo-n-nonoylaspartic Acid,*  
 $\text{C}_8\text{H}_{16}\text{Br}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}.$

5.2 Grams of aspartic acid (1 mol.) dissolved in 80 c.c. of *N*-sodium hydroxide (2 mols.) when treated in the same way as described for  $\alpha$ -bromo-n-nonoylglycine with 10 grams of  $\alpha$ -bromo-n-nonoyl chloride (1 mol.) and 40 c.c. of *N*-sodium hydroxide (1 mol.), and afterwards acidified with hydrochloric acid, yield an oily precipitate of impure  $\alpha$ -bromo-n-nonoylaspartic acid. The oil is extracted with ether, the latter evaporated at the ordinary temperature, the residual oil kept for a few hours in a vacuum desiccator, and finally the  $\alpha$ -bromo-n-nonoylaspartic acid is precipitated by light petroleum. The product (7.5 grams) is collected quickly, washed with light petroleum, and crystallised from hot water, separating in prismatic needles, which melt and decompose at 153–155°. The crystals are moderately soluble in water, readily so, in alcohol, ether, ethyl acetate, ammonia, or alkalis, but they are almost insoluble in benzene or light petroleum:

0.4175 gave 0.0630  $\text{AgBr}$ .  $\text{Br}=22.81$ .

$\text{C}_{13}\text{H}_{22}\text{O}_5\text{NBr}$  requires  $\text{Br}=22.70$  per cent.

*$\alpha$ -Amino-n-nonoylaspartic Acid,*  
 $\text{NH}_2\cdot\text{C}_8\text{H}_{16}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}.$

One gram of  $\alpha$ -bromo-n-nonoylaspartic acid, when treated with aqueous ammonia in the same way as described for  $\alpha$ -bromo-n-nonoylglycine, yields 0.8 gram of  $\alpha$ -amino-n-nonoylaspartic acid, which crystallises from alcohol in monoclinic needles, melting and decomposing at 231–234°. The dipeptide is very soluble in hot or cold water, but only sparingly so in hot, and almost insoluble in cold, absolute alcohol. It is also readily soluble in ammonia, sodium hydroxide, or mineral acids. When dissolved in very dilute sulphuric acid, it gives a white, amorphous precipitate with an aqueous solution of phosphotungstic acid:

0.1804 gave 0.3573  $\text{CO}_2$  and 0.1356  $\text{H}_2\text{O}$ .  $\text{C}=54.03$ ;  $\text{H}=8.41$ .

0.1610 „ 14.0 c.c.  $\text{N}_2$  at 21.4° and 758 mm.  $\text{N}=10.06$ .

$\text{C}_{13}\text{H}_{24}\text{O}_4\text{N}_2$  requires  $\text{C}=54.13$ ;  $\text{H}=8.39$ ;  $\text{N}=9.72$  per cent.

*Action of Ferments on  $\alpha$ -Amino-n-nonoylglycine.*

Pancreatic juice activated by kinase, pancreatin (Defresne), trypsin (Merck), or liver extract appears to have no action on

$\alpha$ -amino-*n*-nonoylglycine. Similarly when micro-organisms, like *Bacillus subtilis* or *Bacillus pyocyaneus*, are cultivated on dilute solutions of peptone rendered slightly alkaline with potassium carbonate and saturated with  $\alpha$ -amino-*n*-nonoylglycine, there is no change in the dipeptide in twenty-four hours. These negative results contrast remarkably with the action of ferments on the corresponding dipeptide,  $\alpha$ -aminolaurylglycine (this vol., p. 576).

In carrying out these biological tests the authors had considerable assistance from Dr. Berthelot, of the Pasteur Institute, Paris.

VICTORIA UNIVERSITY,  
MANCHESTER.



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\* From bottom.

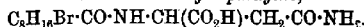
$\alpha$ -nonoylglycine, yield 1.5 grams of  $\alpha$ -amino-*n*-nonoyl-leucine, which crystallises from alcohol in small, prismatic needles, mixed with a few rhombic plates. When heated rapidly, it softens at 234°, and melts and decomposes at 237—238°. The dipeptide is sparingly soluble in water, moderately so in dilute or absolute alcohol, and readily so in ammonia, alkali hydroxides, or mineral acids. When dissolved in dilute sulphuric acid, it yields a white, amorphous precipitate with an aqueous solution of phosphotungstic acid, which is soluble in excess of the reagent:

0.1612 gave 0.3709 CO<sub>2</sub> and 0.1569 H<sub>2</sub>O. C=62.75; H=10.89.

0.1186 " 9.8 c.c. N<sub>2</sub> at 22.2° and 773.5 mm. N=9.73.

C<sub>15</sub>H<sub>30</sub>O<sub>3</sub>N<sub>2</sub> requires C=62.87; H=10.56; N=9.79 per cent.

*$\alpha$ -Bromo-*n*-nonoylasparagine,*

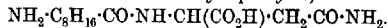


5.9 Grams of *l*-asparagine (1 mol.) dissolved in 40 c.c. of *N*-sodium hydroxide (1 mol.) treated in the cold as described for  $\alpha$ -bromo-*n*-nonoylglycine with 10 grams of  $\alpha$ -bromo-*n*-nonoyl chloride (1 mol.) and 40 c.c. of *N*-sodium hydroxide (1 mol.), and afterwards acidified with dilute hydrochloric acid, yield 14.0 grams of impure  $\alpha$ -bromo-*n*-nonoylasparagine. The product crystallises from absolute alcohol in rhombic prisms, which melt and decompose at 163—164°. The crystals are moderately soluble in hot, but sparingly so in cold, water. They are only moderately soluble in cold, but readily soluble in hot, dilute or absolute alcohol. They are also readily soluble in cold ammonia or alkalis, but are insoluble in ether or benzene:

0.1486 gave 0.0801 AgBr. Br=22.94.

C<sub>13</sub>H<sub>23</sub>O<sub>4</sub>N<sub>2</sub>Br requires Br=22.76 per cent.

*$\alpha$ -Amino-*n*-nonoylasparagine,*



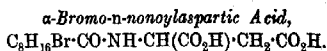
One gram of  $\alpha$ -bromo-*n*-nonoylasparagine, when treated with aqueous ammonia in the same way as described for  $\alpha$ -bromo-*n*-nonoylglycine, yields 0.5 gram of  $\alpha$ -amino-*n*-nonoylasparagine, which crystallises from absolute alcohol containing a few drops of ammonia in fine needles. It sinters at 236° and melts sluggishly, and decomposes at 251—256°. The dipeptide is only sparingly soluble in water or alcohol, but readily so in ammonia, alkali hydroxides, or mineral acids. When dissolved in dilute sulphuric acid, it yields a white, amorphous precipitate with an aqueous solution of phosphotungstic acid, which is soluble in excess of the reagent:

# 1544 SYNTHESIS OF POLYPEPTIDES OF $\alpha$ -AMINO-N-NONOIC ACID.

0.1670 gave 0.3316  $\text{CO}_2$  and 0.1328  $\text{H}_2\text{O}$ .  $\text{C}=54.16$ ;  $\text{H}=8.90$ .

0.2544 „ 32.0 c.c.  $\text{N}_2$  at 22.7 and 756.9 mm.  $\text{N}=14.46$ .

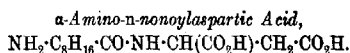
$\text{C}_{13}\text{H}_{25}\text{O}_4\text{N}_2$  requires  $\text{C}=54.30$ ;  $\text{H}=8.77$ ;  $\text{N}=14.63$  per cent.



5.2 Grams of aspartic acid (1 mol.) dissolved in 80 c.c. of *N*-sodium hydroxide (2 mols.) when treated in the same way as described for  $\alpha$ -bromo-*n*-nonoylglycine with 10 grams of  $\alpha$ -bromo-*n*-nonoyl chloride (1 mol.) and 40 c.c. of *N*-sodium hydroxide (1 mol.), and afterwards acidified with hydrochloric acid, yield an oily precipitate of impure  $\alpha$ -bromo-*n*-nonoylaspartic acid. The oil is extracted with ether, the latter evaporated at the ordinary temperature, the residual oil kept for a few hours in a vacuum desiccator, and finally the  $\alpha$ -bromo-*n*-nonoylaspartic acid is precipitated by light petroleum. The product (7.5 grams) is collected quickly, washed with light petroleum, and crystallised from hot water, separating in prismatic needles, which melt and decompose at  $153.5\text{--}155.5^\circ$ . The crystals are moderately soluble in water, readily so in alcohol, ether, ethyl acetate, ammonia, or alkalis, but they are almost insoluble in benzene or light petroleum:

0.1175 gave 0.0630  $\text{AgBr}$ .  $\text{Br}=22.81$ .

$\text{C}_{13}\text{H}_{22}\text{O}_4\text{NBr}$  requires  $\text{Br}=22.70$  per cent.



One gram of  $\alpha$ -bromo-*n*-nonoylaspartic acid, when treated with aqueous ammonia in the same way as described for  $\alpha$ -bromo-*n*-nonoylglycine, yields 0.8 gram of  $\alpha$ -amino-*n*-nonoylaspartic acid, which crystallises from alcohol in monoclinic needles, melting and decomposing at  $231\text{--}234^\circ$ . The dipeptide is very soluble in hot or cold water, but only sparingly so in hot, and almost insoluble in cold, absolute alcohol. It is also readily soluble in ammonia, sodium hydroxide, or mineral acids. When dissolved in very dilute sulphuric acid, it gives a white, amorphous precipitate with an aqueous solution of phosphotungstic acid:

0.1804 gave 0.3573  $\text{CO}_2$  and 0.1356  $\text{H}_2\text{O}$ .  $\text{C}=54.03$ ;  $\text{H}=8.41$ .

0.1610 „ 14.0 c.c.  $\text{N}_2$  at  $21.4^\circ$  and 758 mm.  $\text{N}=10.06$ .

$\text{C}_{13}\text{H}_{24}\text{O}_5\text{N}_2$  requires  $\text{C}=54.13$ ;  $\text{H}=8.39$ ;  $\text{N}=9.72$  per cent.

## *Action of Ferments on $\alpha$ -amino-n-nonoylglycine.*

Pancreatic juice activated by kinase, pancreatin (Defresne), trypsin (Merck), or liver extract appears to have no action on

$\alpha$ -amino- $n$ -nonoylglycine. Similarly when micro-organisms, like *Bacillus subtilis* or *Bacillus pyocyaneus*, are cultivated on dilute solutions of peptone rendered slightly alkaline with potassium carbonate and saturated with  $\alpha$ -amino- $n$ -nonoylglycine, there is no change in the dipeptide in twenty-four hours. These negative results contrast remarkably with the action of ferments on the corresponding dipeptide,  $\alpha$ -aminolaurylglycine (this vol., p. 576).

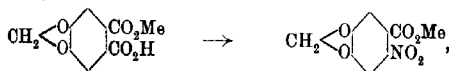
In carrying out these biological tests the authors had considerable assistance from Dr. Berthelot, of the Pasteur Institute, Paris.

VICTORIA UNIVERSITY,  
MANCHESTER.

LXXIX.—*Substitution in Aromatic Hydroxy-compounds. Part I. The Action of Nitric Acid on Gallic Acid Trimethyl Ether and Pyrogallol-carboxylic Acid Trimethyl Ether.*

By VICTOR JOHN HARDING.

It has been known for a long time that many benzenecarboxylic acids containing hydroxy-groups or their ethers when treated with nitric acid give rise to nitro-compounds in which the carboxyl group has been displaced by a nitro-group. Such well-known examples are veratric acid (Tiemann, *Ber.*, 1876, **9**, 939), piperonylic acid (Jobst and Hesse, *Annalen*, 1879, **199**, 70), gallic acid trimethyl ether (Schiffer, *Ber.*, 1892, **25**, 721), and myristicinic acid (Salway, *Trans.*, 1909, **95**, 1165). It has been observed by Oertly and Pictet (*Ber.*, 1910, **43**, 1336) that methyl hydrogen hydrastate when treated with concentrated nitric acid in acetic acid solution gives methyl nitropiperonylate:



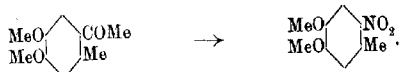
also that bromopiperonylic acid under the same conditions yields bromonitromethylenedioxybenzene:



In order to prevent this displacement of the carboxyl group it has so far been found necessary to make use of the alkyl salts when preparing the desired nitro-acid (compare Hamburg, *Monatsh.*, 1898, **19**, 599; Pollak and Feldscharek, *ibid.*, 1908, **29**, 139).

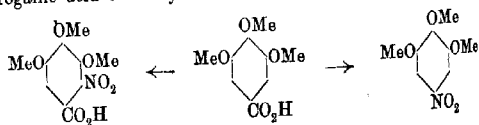
Two years ago Salway (*Trans.*, 1909, **95**, 1155) found that the ethers of aromatic hydroxy-aldehydes when acted on by concentrated nitric acid in the cold also underwent a similar reaction, the aldehyde group in part being displaced by the nitro-group. Piperonal, veratraldehyde, and myristicinaldehyde gave varying amounts of the corresponding nitrophenol ethers as well as the expected nitro-aldehydes. Anisaldehyde, however, only gave nitro-anisaldehyde, and Salway pointed out that the accumulation of methoxyl groups resulted in an increased displacement of the formyl grouping.

That acetyl groups could be similarly displaced was observed by Harding and Weizmann (*Trans.*, 1910, **97**, 1126), who by acting on 4:5-dimethoxy-*o*-methylacetophenone with nitric acid in warm glacial acetic acid solution obtained nitrohomocatechol dimethyl ether:



It was evident that these peculiar displacements were of more general occurrence than had formerly been supposed, and it was thought desirable to investigate the phenomena more closely, in order to see if any generalisation were possible, and also whether any means could be found of inhibiting the reaction, thus rendering possible the production in an easy and simple manner of the apparently more normal nitration products. In this connexion a careful study of the action of nitric acid on gallic acid trimethyl ether and the isomeric pyrogallolcarboxylic acid trimethyl ether has brought to light some interesting points.

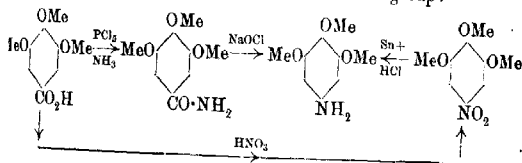
The action of nitric acid on gallic acid trimethyl ether has been investigated by Schiffer (*Ber.*, 1892, **25**, 721), who observed the displacement of the carboxyl group. Quite recently, and between the experimental results of the author and their publication, then appeared the communication of Thoms and Siebeling (*Ber.*, 1911, **44**, 2115) on the same subject. A thoroughly exhaustive examination of the products, however, does not appear to have been attempted. The action of nitric acid at 50–70°, the acid being either concentrated (D 1.4) or dilute, or in acetic acid solution, always gives a mixture of 5-nitropyrogallol trimethyl ether and nitrogallic acid trimethyl ether:



The largest yields of 5-nitropyrogallol trimethyl ether are obtained in acetic acid solution, and it is worthy of note that many of these displacements take place most readily when the nitration is carried out in that solvent. Thoms and Siebeling (*loc. cit.*), using fuming nitric acid in acetic acid solution, found that at  $-15^{\circ}$  the chief product was 5-nitropyrogallol trimethyl ether, whilst on warming 5:6-dinitropyrogallol trimethyl ether was obtained, nitration of the previously-formed mononitro-compound evidently taking place. The author has also found what is probably 5:6-dinitropyrogallol trimethyl ether among the nitration products. The compound melted at  $113^{\circ}$  (Thoms and Siebeling give  $119^{\circ}$ ), and was insoluble in dilute alkalis. The point, however, is being re-investigated. It does not appear to have been previously observed that nitrogalllic acid trimethyl ether is formed by the direct nitration of gallic acid trimethyl ether. The acid, however, has been prepared by Poliak and Feldscharek (*Monatsh.*, 1908, **29**, 135) by the hydrolysis of its ethyl ester, and again in exactly the same way by Thoms and Siebeling.

In addition to the above-mentioned compounds, there was isolated large amounts of oxalic acid, a dibasic acid,  $C_{18}H_{17}O_{13}N$ , and a very small amount of an acid melting at  $154.5^{\circ}$ . The question of the displacement of methoxyl groups by nitro-groups was also considered, but no evidence was obtainable that any such displacement had taken place.

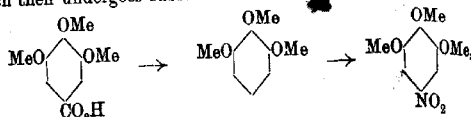
The orientation of 5-nitropyrogallol trimethyl ether was accomplished by Graebe and Suter (*Annalen*, 1905, **340**, 222), thus proving that the nitro-group had displaced the carboxyl group, and that it had not arisen from the nitrogalllic acid trimethyl ether by the elimination of carbon dioxide. The following scheme shows quite clearly the proof of the position of the nitro-group:



The present author has repeated this work, and confirmed it. In addition, two specimens of 5-acetylaminopyrogallol trimethyl ether were prepared from specimens of the base obtained by the two methods indicated in the diagram, and were found to be identical. Thus there can be no doubt that the action of nitric acid on gallic acid trimethyl ether results in the displacement of the carboxyl group by the nitro-group.

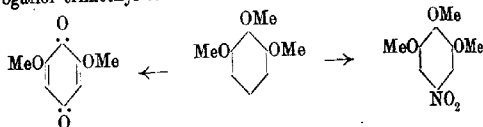


In considering displacements of groups of this kind by nitric acid, one obvious explanation suggests itself, namely, that the organic acid loses carbon dioxide, forming the parent phenol ether, which then undergoes substitution in the usual way:



and in the case of aldehydes and ketones that the side-chains, formyl and acetyl, undergo a preliminary oxidation to carboxyl. This view is borne out by the fact that carboxyl groups do not undergo this substitution. Salway (*loc. cit.*, p. 1159), however, has pointed out that, in the case of aldehydes, this view is untenable, and a consideration of the products of nitration of gallic acid trimethyl ether apparently points to the fact that it is also inadmissible in the case of organic acids, if gallic acid trimethyl ether can be taken as representative of this class of reaction.

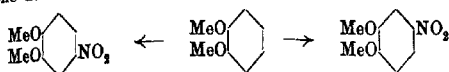
The action of nitric acid on pyrogallol trimethyl ether gives rise to a mixture of 3:5-dimethoxy-*p*-benzoquinone, as well as 5-nitropyrogallol trimethyl ether:



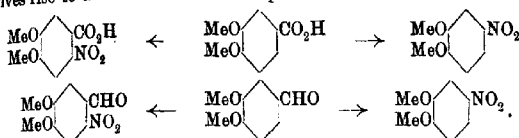
(Will, *Ber.*, 1888, **21**, 613; Schiffer, *Ber.*, 1892, **25**, 725; Graebe and Hess, *Annalen*, 1905, **340**, 232; Pollak and Goldstein, *Monatsh.*, 1908, **29**, 137). Formation of 3:5-diethoxy-*p*-benzoquinone also occurs during the nitration of pyrogallol triethyl ether (Pollak and Goldstein, *Monatsh.*, 1908, **29**, 137). If, then, there is during the production of 5-nitropyrogallol trimethyl ether from gallic acid trimethyl ether any intermediate formation of pyrogallol trimethyl ether, as such, it would be expected to show itself by the occurrence of 3:5-dimethoxy-*p*-benzoquinone among the products of nitration. This, however, is not the case; a most exhaustive search failed to reveal the presence of this quinone. Schiffer also states that the nitration of gallic acid trimethyl ether produces no quinone. It may be concluded then that the course of these reactions is one of direct substitution of the carboxyl or aldehyde group by the nitro-group.

In studying the rather scanty literature of reactions of this type it was noticed that the substitution of the acyl group always gave rise to the same nitrophenol ether as that produced by the nitration

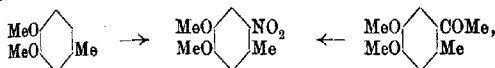
of the phenol ether itself. This is very clearly brought out if the substitution of veratrole is compared with that of its derivatives, veratric acid and veratraldehyde. The nitro-group enters either at the positions 4 or 5. In the case of veratrole this gives rise to the one derivative, 4- or 5-nitroveratrole:



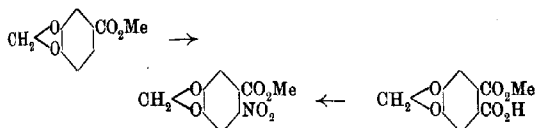
whereas in veratroles already substituted in positions 4 or 5 it gives rise to a mixture of nitro-compounds:



Homocatechol dimethyl ether and its ketone, 4:5-dimethoxy-*o*-methylacetophenone, give the same nitrohomocatechol dimethyl ether:



also methyl piperonylate and methyl hydrogen hydrastate show a similar behaviour:

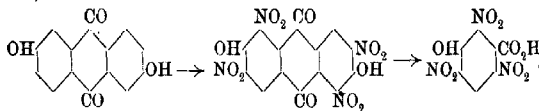


It would seem very probable from these examples that the substitution of acyl groupings by the nitro-group is conditioned by those forces in the molecule which direct the entrance of a nitro-group in the parent phenol ether, and that the substitution of the more complex group differs only in degree from that of hydrogen. That equal amounts of nitroveratric acid and nitroveratrole are not produced by the nitration of veratric acid is due to the more mobile hydrogen atom being more easily substituted than the heavier carboxyl. It must not be forgotten, however, that the carboxyl group itself exerts a definite directive influence as against that of the hydrogen atoms, but it would appear that its influence is small when compared with that of the methoxyl groups. The directive power of the two methoxyl groups in veratrole would appear to be sufficiently powerful to suppress that of certain other substi-

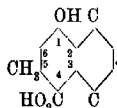
tments, and to cause substitution to take place in the manner described.

One consequence of the displacement of acyl groups being similar to that of hydrogen is that the substitution of the more complex groups should obey those laws which govern the ordinary substitution in the benzene ring. Just as the action of nitric acid on the hydrogen atoms of substituted benzenes results in a selective action, and by doing so has given rise to the well known ortho-, para-, and meta-rules of substitution, so ought this selective action to be observed when the more complex groups are substituted. Thus, if the carboxyl group, etc., occupies a position which would not be substituted by a nitro-group in the parent phenol ether, then that group will be inactive towards nitric acid. Cases in which the action of nitric acid has been studied in this way are few in number, and are confined to derivatives of phenol.

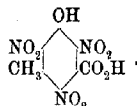
The positions in phenol reactive to nitric acid are the positions 2:4:6. Consequently it would be expected that groups occupying the positions 2:4:6 would be substituted by the nitro-group, and that those occupying the inactive positions 3:5 would remain unsubstituted; and this is found to be the case. Salicylic acid on continued nitration yields picric acid, the lighter and more mobile hydrogen atoms being first displaced, and finally the carboxyl group itself (Hübner, *Annalen*, 1879, **195**, 31; Hübner, Babcock, and Schaumann, *Ber.*, 1879, **12**, 1346; Schiff and Nasino, *Annalen*, 1879, **198**, 258; see also Beilstein, *Handbuch*, IV., 1490). Coumarin in a similar manner gives picric acid (Delaude, *Annalen*, 1843, **45**, 337), and derivatives of *p*-coumaric acid also on nitration yield *s*-trinitrophenol, for example, carthamine (Kametaka and Perkin, *Trans.*, 1910, **97**, 1419). On the other hand, anthraflavic acid on nitration gives tetranitroanthraflavic acid, and finally 2:4:6-trinitro-*m*-hydroxybenzoic acid (Scharfing, *Ber.*, 1875, **8**, 1490):



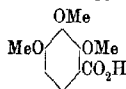
A still more striking example is the action of nitric acid on carminic acid, which contains the groupings:



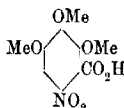
The groups occupying the active positions 2:4:6 are substituted by nitro-groups, either direct or after oxidation, whilst groups in the inactive positions 3:5 remain unsubstituted, and give rise to trinitrohydroxy-*m*-toluic acid (Kostanecki and Niementowski, *Ber.*, 1885, **18**, 253):



In order to gain more evidence on this important point it was deemed advisable to select a compound in which a carboxyl or aldehyde group occupied an inactive position in a molecule containing a large number of methoxyl groups, and to investigate the action of nitric acid on it under varying conditions. The presence of a large number of methoxyl groups would cause the carboxyl or aldehyde group to be more sensitive to the action of nitric acid (compare Salway, *loc. cit.*, p. 1159), and thus it would be possible to determine easily whether any substitution had taken place. The compound chosen was pyrogallolcarboxylic acid trimethyl ether (I):



(I.)

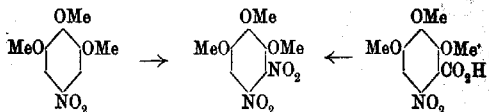


(II.)

The action of nitric acid on this compound does not appear to have been previously studied. The nitro-acid (II), however, has been prepared by Poilak and Goldstein (*Annalen*, 1907, **351**, 161) by nitrating methyl pyrogallolcarboxylate trimethyl ether, with subsequent hydrolysis.

The action of concentrated nitric acid in the cold, either alone or in acetic acid solution, results in the formation in almost quantitative yield of nitropyrogallolcarboxylic acid trimethyl ether. The use of the methyl ester of pyrogallolcarboxylic acid to prevent any possible carboxyl substitution taking place is unnecessary. The product obtained direct from the nitration of the free acid was completely soluble in sodium carbonate, and possessed the correct melting point. When, however, the action of hot nitric acid was investigated, it was found that a very small amount of a neutral substance was obtained, in addition to the nitro-acid. This melted at 118°, and was in all probability (see p. 1596) 5:6-dinitropyrogallol trimethyl ether. No trace of 6-nitropyrogallol trimethyl ether was observed. This compound has been prepared by Einhorn, Cobliner, and Pfeiffer (*Ber.*, 1904, **37**, 117), and melts at 44°

(compare also Thoms and Siebeling, *loc. cit.*) The formation of 5:6-dinitropyrogallol trimethyl ether is in accordance with the views expressed in this paper; the carboxyl group in nitropyrogallolcarboxylic acid trimethyl ether occupies the position in 5-nitropyrogallol trimethyl ether active towards a nitro-group, and is in consequence substituted:



whereas when not occupying the inactive position as in pyrogallolcarboxylic acid trimethyl ether, it remains unaffected by the nitric acid, although the isomeric gallic acid trimethyl ether undergoes substitution in a very marked manner.

It would seem very probable, then, by these examples that the substitution of acyl groups is governed by the same forces in the benzene nucleus which control the substitution of the hydrogen atoms in the parent phenol ether. The groups  $\cdot\text{H}$ ,  $\cdot\text{CHO}$ ,  $\cdot\text{CO}$ ,  $\cdot\text{CH}_3$ ,  $\cdot\text{CO}_2\text{H}$  apparently form a series, any member of which can be substituted by the group  $\cdot\text{NO}_2$ . It remains to be seen how far this series can be extended, and work is in progress to determine this point. As regards the actual mechanism of the substitutions, it is of interest to note that if the nitrations are carried out in the cold in presence of a trace of hydrogen peroxide, the expected substitution does not take place. Gallic acid trimethyl ether, on treatment with concentrated nitric acid in presence of a trace of hydrogen peroxide, does not yield any 5-nitropyrogallol trimethyl ether. This interesting observation, which may turn out to be of great practical utility, is at present being studied, and the results will shortly be laid before the Society.

#### EXPERIMENTAL.

##### *Action of Nitric Acid on Gallic Acid Trimethyl Ether.*

In order to investigate thoroughly the action of nitric acid on gallic acid trimethyl ether, and to observe if any formation of 3:5-dimethoxy-*p*-benzoquinone occurred, the reaction was carried out under the following conditions.

I.—Fifty grams of gallic acid trimethyl ether were added in small quantities at a time to 100 c.c. of concentrated nitric acid (D 1.4). A vigorous reaction took place with rise of temperature, carbon dioxide and nitrous fumes being rapidly evolved. The temperature, however, was not allowed to rise above 50°. When

all the gallic acid trimethyl ether had been added, the reaction was completed by allowing the mixture to remain at room temperature for an hour. It was then diluted with water, and the precipitated substances were collected. The 5-nitropyrogallol trimethyl ether (A) was purified from the accompanying carboxylic acids by dissolving the latter in dilute sodium carbonate solution, and washing the residue well with water. In this way there was obtained 9.5 grams of 5-nitropyrogallol trimethyl ether. The sodium carbonate washings on acidification yielded 7 grams of an acid mixture (B) (p. 1595).

II.—Gallic acid trimethyl ether was heated with dilute nitric acid (1:4) until the vigorous reaction which set in had subsided. In this case the temperature was not allowed to rise above 70°. The solid products which separated on cooling were collected, and treated as described in method I. Fifty grams of gallic acid trimethyl ether in this manner gave 11 grams of crude 5-nitropyrogallol trimethyl ether (A) and 2 grams of an acid mixture (B).

III.—In this case gallic acid trimethyl ether was dissolved in glacial acetic acid, and an excess of nitric acid added. The reaction again was very vigorous, but the yield of neutral compounds obtained on dilution was much larger under these conditions. From 50 grams of gallic acid trimethyl ether were obtained 26 grams of crude neutral compounds (A) and 8 grams of an acid mixture (B).

The filtrates (C) from these nitration experiments were mixed and investigated as described on page 1596.

#### *Examination of 5-Nitropyrogallol Trimethyl Ether (A).*

The whole of the crude 5-nitropyrogallol trimethyl ether obtained from the above-described experiments was purified by crystallisation from absolute alcohol, from which it separated quite readily in the characteristic pale yellow needles, melting at 99°. The residues on complete evaporation of the alcohol yielded a small amount of a substance, which when crystallised from dilute acetic acid melted at 88–89°. When freshly prepared it consisted of almost colourless needles, which on drying and exposure to light were converted into a yellow, amorphous-looking powder. The amount, however, was too small to permit of further investigation, and it is very doubtful if a pure substance was isolated.

#### *Gallamide Trimethyl Ether, $C_6H_2(OMe)_3 \cdot CO \cdot NH_2$ .*

This compound has been previously prepared by the methylation of gallamide (Marx, *Annalen*, 1891, 263, 250), and by passing dry

ammonia gas into a benzene solution of gallyl chloride trimethyl ether (Graebe and Suter, *Annalen*, 1905, **340**, 222). Its preparation, however, is easily effected by pouring a large excess of concentrated aqueous ammonia on to freshly prepared powdered gallyl chloride trimethyl ether, when the amide separates as a white, insoluble solid. It is collected, washed with cold water, and purified by crystallisation from 90 per cent. alcohol. It melts at 157°. (Found, N=6.7. Calc., N=6.6 per cent.)

*5-Acetylaminopyrogallol Trimethyl Ether,*  
 $C_6H_2(OMe)_3 \cdot NH \cdot CO \cdot CH_3$ .

The base 5-aminopyrogallol trimethyl ether was prepared (a) by the action of freshly prepared sodium hypochlorite on gallamide trimethyl ether (Graebe and Suter, *Annalen*, 1905, **340**, 222); (b) by the reduction of 5-nitropyrogallol trimethyl ether (Will, *Ber.*, 1888, **21**, 613).

A mixed melting-point determination made with specimens of the base prepared by both methods gave the same melting point as that shown by each constituent. 5-Acetylaminopyrogallol trimethyl ether is easily obtained by warming the base with acetic anhydride on the water-bath for an hour, cooling, and then pouring into water. It crystallises from alcohol in small needles, which soften at 110°, and finally melt at 127°, and contains one molecule of water of crystallisation:

0.1354 gave 0.2676  $CO_2$  and 0.0812  $H_2O$ . C=53.9; H=6.6.

0.1434 „ 7.5 c.c.  $N_2$  (moist) at 20° and 756 mm. N=5.9.

$C_{11}H_{15}O_4N \cdot H_2O$  requires C=54.3; H=6.9; N=5.7 per cent.

A direct determination of the water of crystallisation does not give a very satisfactory result, as even when kept at 100° there is considerable decomposition if the heating is continued for any length of time. The figures, however, show the presence of one molecule of water of crystallisation if the rate of the loss of water is taken into account:

0.2997, on heating at 101° for one hour, lost 0.0214.

0.2997, „ „ 101° „ two hours, „ 0.0224.

Loss at end of first hour=7.2 per cent.

„ „ second „ =8.2 „ \*

$C_{11}H_{15}O_4N \cdot H_2O$  requires loss=7.4 per cent. \*

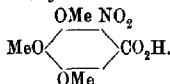
The acetyl group is not hydrolysed by warm dilute aqueous potassium hydroxide.

The same acetyl derivative is produced from specimens of base prepared by either methods (a) or (b). This was confirmed by the

method of mixed melting point. Graebe and Suter (*loc. cit.*) give the melting point of 5-acetylaminopyrogallol trimethyl ether as  $124^{\circ}$ , but no analysis of their product is given.

*Examination of the Acid Mixture (B).*

*Isolation of Nitrogallie Acid Trimethyl Ether,*



The crude acid mixtures from the three previously described nitration experiments (p. 1593) were mixed together, and the nitrogallie acid trimethyl ether was separated from its accompanying impurities by crystallisation from benzene, it being almost insoluble in the cold solvent. It was identified by means of its melting point ( $163\text{--}164^{\circ}$ ) and analysis. (Found,  $\text{C}=46.7$ ;  $\text{H}=4.1$ . Calc.,  $\text{C}=46.6$ ;  $\text{H}=4.2$  per cent.)

This acid has previously been described by Pollak and Feldscharek (*Monatsh.*, 1908, **29**, 139), who obtained it by the hydrolysis of its ethyl ester, a compound prepared by the nitration of ethyl gallate trimethyl ether. It seems, however, to have escaped observation that it is one of the products of the direct nitration of gallic acid trimethyl ether.

Nitrogallie acid trimethyl ether is esterified only with great difficulty.

*Nitrogallamide trimethyl ether* is readily prepared by mixing nitrogallie acid trimethyl ether with a small excess of phosphorus pentachloride in presence of a little benzene and warming slightly. A gentle reaction sets in, and at the end of two hours the semi-solid mass is poured into a large excess of concentrated aqueous ammonia, when the amide separates as a solid mass. It crystallises from alcohol in pulpy masses of needles, melting at  $182\text{--}184^{\circ}$ :

0.1339 gave 0.2323  $\text{CO}_2$  and 0.0529  $\text{H}_2\text{O}$ .  $\text{C}=47.3$ ;  $\text{H}=4.4$ .

$\text{C}_{10}\text{H}_{12}\text{O}_6\text{N}_2$  requires  $\text{C}=46.9$ ;  $\text{H}=4.6$  per cent.

*Isolation of an Acid,  $\text{C}_{18}\text{H}_{17}\text{O}_{13}\text{N}$ .*

The benzene mother liquors from the separation of the nitrogallie acid trimethyl ether were evaporated to a small bulk, and an equal volume of light petroleum was added. The yellow precipitate which formed was collected and purified by crystallisation from water until further crystallisation ceased to alter its melting point. The acid separates from water in almost colourless nodules, which rapidly turn yellow on exposure to light, and melt at  $136\text{--}137^{\circ}$ :



0.1297 gave 0.2245  $\text{CO}_2$  and 0.0435  $\text{H}_2\text{O}$ .  $\text{C}=47.2$ ;  $\text{H}=3.7$ .

0.1591 „ 4.8 c.c.  $\text{N}_2$  (moist) at  $24^\circ$  and 756 mm.  $\text{N}=3.3$ .

$\text{C}_{18}\text{H}_{17}\text{O}_{13}\text{N}$  requires  $\text{C}=47.5$ ;  $\text{H}=3.9$ ;  $\text{N}=3.1$  per cent.

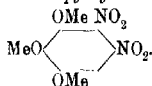
A determination of the basicity gave the following results:

0.1307 required for neutralisation 0.0223  $\text{NaOH}$ , whilst the same weight of a dibasic acid,  $\text{C}_{18}\text{H}_{17}\text{O}_{13}\text{N}$ , requires 0.0227  $\text{NaOH}$ .

#### *Examination of the Filtrate (C).*

The aqueous residues from the nitration of gallic acid trimethyl ether, amounting to about two litres, were combined and evaporated on the water-bath to about half their bulk, and then set aside in a cold air chamber to crystallise. After keeping overnight, a mass of crystals separated, which on collection was found to consist of oxalic acid mixed with a small amount of the acid,  $\text{C}_{18}\text{H}_{17}\text{O}_{13}\text{N}$  (p. 1595), the two acids being easily separated by means of warm water. A further evaporation and cooling resulted in the separation of more oxalic acid, but in this case free from the acid  $\text{C}_{18}\text{H}_{17}\text{O}_{13}\text{N}$ . In all, there were isolated about forty grams of oxalic acid.

#### *Isolation of 5:6-Dinitropyrogallol Trimethyl Ether,*



The remaining nitric acid was then removed by repeated evaporation and dilution, when there gradually separated a very small amount of a colourless, flocculent precipitate. This, on crystallisation from alcohol or acetic acid, melted constantly at  $118^\circ$ , and any further treatment failed to alter its properties. Thoms and Siebeling give the melting point of 5:6-dinitropyrogallol trimethyl ether as  $119^\circ$ , and state that the melting point given by Will ( $126^\circ$ ) is too high. As the compound (m. p.  $118^\circ$ ) agreed in properties with the 5:6-dinitropyrogallol trimethyl ether described by Thoms and Siebeling (*Ber.*, 1911, **44**, 2123), this, taken in conjunction with the method of preparation and the fact that the same compound is also formed by the action of hot nitric acid on pyrogallolcarboxylic acid trimethyl ether (see p. 1597), is taken provisionally as evidence of its constitution. The point, however, will be re-investigated.

*Isolation of an Acid Melting at  $154.5^\circ$ .*—The residues after the separation of the above-described substance were evaporated to dryness, triturated with cold sodium carbonate solution, and

filtered. The filtrate on acidifying slowly deposited a small quantity of an acid, which after two crystallisations from water melted sharply at  $154.5^{\circ}$ . The amount, however, was too small to permit of further investigation.

Thus from 150 grams of gallic acid trimethyl ether there was obtained nearly 110 grams of products, and a most exhaustive search had failed to detect the presence of 3:5-dimethoxy-*p*-benzoquinone, even in the slightest trace. Under conditions identical with those obtaining in the experiments just described, the action of nitric acid on pyrogallol trimethyl ether yielded large amounts of this quinone (compare Graebe and Hess, *Annalen*, 1905, **340**, 232).

*Action of Nitric Acid on Pyrogallolcarboxylic Acid Trimethyl Ether.*

The action of nitric acid on pyrogallolcarboxylic acid trimethyl ether was studied under the following conditions:

I.—Two grams of acid were dissolved in excess of concentrated nitric acid, and the solution kept cold by a stream of water. There is no violent reaction, as in the case of gallic acid trimethyl ether. At the end of fifteen minutes water was added, and the clear liquid was allowed to remain for some hours in the cold air chamber, when there slowly separated a mass of faintly yellow crystals. These were found to be completely soluble in cold dilute sodium carbonate solution, and a melting-point determination showed them to consist of pure nitropyrogallolcarboxylic acid trimethyl ether.

II.—Two grams of the acid were dissolved in acetic acid, and to this solution was added the nitric acid, the whole being allowed to remain at room temperature for fifteen minutes. The crystalline product which separated on dilution was found to consist entirely of nitropyrogallolcarboxylic acid trimethyl ether. No neutral compounds were observed.

III.—The action of hot concentrated nitric acid on pyrogallolcarboxylic acid trimethyl ether, however, results in the production of a very small amount of a substance insoluble in cold dilute sodium carbonate solution, as well as the nitro-acid. From two grams of pyrogallolcarboxylic acid trimethyl ether there was obtained enough neutral substance to permit of its crystallisation and a determination of the melting point. It crystallised from alcohol in colourless needles, melting at  $118^{\circ}$ , and was found to be identical with the 5:6-dinitropyrogallol trimethyl ether obtained by the nitration of gallic acid trimethyl ether (p. 1596).

The aqueous residues from the above experiments were mixed together and evaporated on the water-bath. These separated from

the solution a further amount of 6-nitropyrogallolcarboxylic acid trimethyl ether. The mother liquors were then completely evaporated, and the small residue was extracted with cold dilute sodium carbonate solution. This on acidifying yielded a small amount of an acid, which softened at 90°, and finally melted at 100°.

In conclusion, I desire to thank the Research Fund Committee of the Chemical Society for the grant which has defrayed the cost of this investigation, and also to thank Dr. J. W. Walker for the kindly interest he has taken during the progress of this work.

MACDONALD CHEMISTRY AND MINING BUILDING,  
MCGILL UNIVERSITY, MONTREAL.

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CLXXX.—*Trialkylammonium Nitrites and Nitrites of the Bases of the Pyridine and Quinoline Series.*  
*Part II.*

By PAÑCHĀNAN NEOGI, M.A.

*α-Picolinium Nitrite.*

AN ice-cold solution of α-picoline hydrochloride was treated with silver nitrite in a bottle immersed in melting ice. The filtered solution did not liberate any iodine on the addition of potassium iodide, but on the addition of an acid, iodine was copiously set free. The volume of nitrogen obtained by the "urea" method was identical with the volume of nitric oxide obtained by the Crum-Frankland method, showing that a pure nitrite was formed in the solution. Very little free nitrous acid was present in the cold solution, as practically no nitrogen was evolved by treating an aliquot part of the liquid with carbamide alone in the Crum nitrometer without the addition of dilute sulphuric acid.

An ice-cold alcoholic solution of the nitrite when evaporated to dryness in a vacuum desiccator over sulphuric acid, surrounded with broken ice, yielded colourless, needle-shaped crystals, which on examination were found to consist of a mixture of α-picolinium nitrite and nitrate.

*Quinolinium Nitrite.*

An ice-cold solution of the nitrite was prepared in the same manner as above. No iodine was set free on the addition of potassium iodide alone, but on the addition of a dilute acid, iodine

was copiously liberated. The cold solution gave equal volumes of nitrogen and nitric oxide by the "urea" and Crum-Frankland methods. A small quantity of nitrogen was collected when an aliquot part of the cold solution was treated with carbamide without the addition of dilute sulphuric acid, showing the presence of very small quantities of free nitrous acid.

An ice-cold solution of the nitrite when evaporated in a vacuum desiccator over sulphuric acid surrounded with broken ice gave a liquid which was found to be quinoline. The nitrite which undoubtedly exists in solution has not been obtained in the solid condition.

*Piperidinium Nitrite,  $C_5H_{11}N, HNO_2$ .*

Ray and Rakshit (Proc., 1911, 27, 71) have prepared dimethylammonium nitrite, a nitrite of a secondary alkylamine. Experiments were undertaken to see if piperidine, a secondary base of the pyridine series, would form a nitrite. The hydrochloride of the base was treated as usual with silver nitrite at the ordinary temperature. The resulting solution was neutral, and copiously liberated iodine on the addition of an acidified solution of potassium iodide. The solution could be concentrated on the water-bath to a small bulk, and when evaporated to dryness in a vacuum desiccator over sulphuric acid yielded colourless plates. The crystals were extremely hygroscopic, very soluble in water or alcohol, but very sparingly so in ether. The salt was fairly stable, and on keeping in the desiccator remained unchanged for a long time. The salt was analysed by the "urea" method:

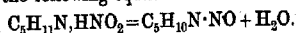
0.4108 gave 76.0 c.c.  $N_2$  (made up to 20 c.c. with water, of which 1 c.c. = 3.8 c.c.  $N_2$ ) at  $27^\circ$  and 750 mm.  $N$ ("nitritic") = 10.05.  
 $C_5H_{11}N, HNO_2$  requires  $N$ ("nitritic") = 10.6 per cent.

*Sublimation and Decomposition of Piperidinium Nitrite.*

The crystals were heated under diminished pressure in a long tube immersed in a sulphuric acid bath. When the temperature was about  $75^\circ$  and the pressure was 10–20 mm., small crystals began to appear in the upper part of the tube. The temperature was kept between  $80^\circ$  and  $100^\circ$ , when the salt slowly sublimed to form a white crust on the upper part of the tube. The sublimed salt was found to be piperidinium nitrite.

When, however, the temperature was raised to  $110^\circ$  the salt began to melt, and at  $120^\circ$  the whole of it was turned into a reddish-yellow liquid. The temperature was raised to  $140^\circ$  in order to ensure the complete decomposition of the nitrite. The liquid was moderately soluble in water, readily gave Liebermann's reaction,

and boiled with charring at about  $215^{\circ}$ . The liquid was thus nitrosopiperidine. The decomposition of piperidinium nitrite is represented by the following equation:



Ray and Rakshit (Proc., 1911, 27, 122) have shown that dimethylammonium nitrite decomposes on heating, forming nitrosodimethylamine, although without sublimation. Piperidinium nitrite was found to volatilise with steam under diminished pressure in appreciable quantities.

*Pyridine Methonitrite,  $\text{C}_5\text{H}_5\text{N}\cdot\text{CH}_3\cdot\text{NO}_2$ .*

The bases of this series form additive compounds with alkyl iodides. The following experiments show that these additive products yield nitrites of a fairly stable character. The iodides should be prepared at the time of the preparation of the nitrites, as otherwise they gradually turn yellow and then red on keeping for some days.

A solution of pyridine methiodide was treated with silver nitrite in the usual manner. The filtered solution was neutral, and liberated iodine copiously from an acidified solution of potassium iodide. The solution could be concentrated to a small bulk on the water-bath, and when kept in a vacuum desiccator over sulphuric acid gave a reddish-yellow liquid, which was found on analysis to be pyridine methonitrite:

0.5404 gave 98.0 c.c.  $\text{N}_2$  (made up to 20 c.c. with water, of which 1 c.c. = 4.9 c.c.  $\text{N}_2$ ) at  $27^{\circ}$  and 752 mm.  $\text{N}$ ("nitritic") = 9.8.

$\text{C}_5\text{H}_5\text{N}\cdot\text{CH}_3\cdot\text{NO}_2$  requires  $\text{N}$ (nitritic) = 10.0 per cent.

The nitrite was very soluble in water or alcohol, and almost insoluble in ether.

*Piperidine Methonitrite,  $\text{C}_5\text{NH}_{11}\cdot\text{CH}_3\cdot\text{NO}_2$ .*

The solution of the nitrite was prepared in the usual manner. It was neutral, and could be concentrated on the water-bath to a small bulk. On evaporating the solution to dryness in a vacuum desiccator over sulphuric acid, the nitrite was obtained in colourless plates:

0.1766 gave 32.0 c.c.  $\text{N}_2$  (made up to 10 c.c. with water, of which 1 c.c. = 3.2 c.c.  $\text{N}_2$ ) at  $28^{\circ}$  and 754 mm.  $\text{N}$ ("nitritic") = 9.8.

$\text{C}_5\text{H}_{11}\text{N}\cdot\text{CH}_3\cdot\text{NO}_2$  requires  $\text{N}$ ("nitritic") = 9.5 per cent.

The crystals were extremely hygroscopic, very soluble in water and alcohol, and sparingly so in ether.

*Isoline Methonitrite*,  $\text{CH}_3\cdot\text{C}_5\text{NH}_7\cdot\text{CH}_3\cdot\text{NO}_2$ .

The solution as prepared in the usual way was colourless, but on evaporation to a small bulk on the water-bath or in a vacuum desiccator over sulphuric acid gave a red liquid, which ultimately solidified to red fibrous crystals. The red colour is due to the presence of an impurity, and the crystals are really colourless:

0.2024 gave 32.0 c.c.  $\text{N}_2$  (made up to 10 c.c. with water, of which 1 c.c. = 3.2 c.c.  $\text{N}_2$ ) at  $27^\circ$  and 750 mm.  $\text{N}$ ("nitritic") = 8.59.

$\text{C}_6\text{H}_7\text{N}\cdot\text{CH}_3\cdot\text{NO}_2$  requires  $\text{N}$ ("nitritic") = 9.09 per cent.

The crystals were very hygroscopic, very soluble in water or alcohol, and insoluble in ether.

*Quinoline Methonitrite*,  $\text{C}_9\text{NH}_7\cdot\text{CH}_3\cdot\text{NO}_2$ .

The solution of this nitrite was at first colourless, but during concentration and exposure to air gradually changed to orange, then red, and finally dark red. The crystals of the same colour obtained in the vacuum desiccator were very hygroscopic, very soluble in water or alcohol, and sparingly so in ether:

0.1540 gave 15.9 c.c.  $\text{N}_2$  at  $27^\circ$  and 750 mm.  $\text{N}$ ("nitritic") = 5.6.

$\text{C}_9\text{H}_7\text{N}\cdot\text{CH}_3\cdot\text{NO}_2$  requires  $\text{N}$ ("nitritic") = 7.3 per cent.

The low value is due to liberation of carbon.

The action of heat on these compounds is being studied, and the examination of other nitrites of this series is being continued.

CHEMICAL LABORATORY, RAJSHAHI COLLEGE,  
RAJSHAHI, EASTERN BENGAL, INDIA.

CLXXXI.—*Ionisation in Non-aqueous Solvents. Part I.*

By HARRY MEDFORTH DAWSON and MAY SYBIL LESLIE, M.Sc.

In this paper an account is given of observations which show the occurrence of unexpected ionisation phenomena in non-aqueous solutions of perhalogen salts. The nature of the solutions, which are obtained when iodides of the alkali metals or ammonium radicles together with iodine are dissolved in nitrobenzene, has already been examined in some detail, and evidence in favour of the existence of definite polyiodides of the types  $\text{MI}_3$ ,  $\text{MI}_5$ ,  $\text{MI}_7$ , and  $\text{MI}_9$  has been adduced (Dawson, Trans., 1908, 93, 1308). Such polyiodide solutions are good conductors of electricity, and by

means of conductivity and freezing-point measurements, the degree of ionisation of the various polyiodides was determined (Dawson and Jackson, *Trans.*, 1908, **93**, 2063).

The collected data for nitrobenzene solutions (*loc. cit.*, p. 2068) indicate that in 0.1 molar solution the conductivity decreases slightly from the tri-iodide to the enne-iodide, the decrease corresponding with the diminishing mobility of the polyiodide anion as its complexity increases. On the other hand, observations made with tetrapropylammonium iodide, which is the only iodide examined which is readily soluble in nitrobenzene, show that the conductivity of the simple iodide is somewhat smaller than that of the corresponding polyiodides. A similar, but much larger, difference was obtained with sodium, ammonium, potassium, rubidium, and caesium iodides when small quantities of ethyl alcohol were added to the nitrobenzene in order to obtain a solvent capable of dissolving the simple iodides sufficiently to yield 0.005 molar solutions.

These observations appeared to warrant a further inquiry into the conductivity and ionisation relationships of the simple and polyiodides in other organic solvents. Measurements of the conductivity have therefore been made in methyl alcohol, ethyl alcohol, methyl acetate, ethyl acetate, benzonitrile, nitromethane, nitrobenzene, and acetic acid solutions. Potassium iodide was chiefly used as electrolyte, although a few measurements were made with tetraethyl- and tetrapropyl-ammonium iodide.

In the following tables the conducting powers of the various solutions at 18° are expressed as molecular conductivities, and values are recorded for solutions in which the molar ratio of iodine to iodide ( $I_2/MI$ ) was respectively 0, 0.5, 1, 2, 3, 4, or some higher number. The solvent, the iodide, and its molar concentration are indicated at the head of each table.

*Methyl Alcohol.*

0.1 Molar potassium iodide.

Ratio $I_2/KI$ .....	0	0.5	1	2	3	4	7
Molecular conductivity...	62.4	66.6	67.0	64.0	60.4	58.9	54.9

0.01 Molar potassium iodide.

Ratio $I_2/KI$ .....	0	0.5	1	2	3	4	7
Molecular conductivity...	82.5	84.4	85.4	84.0	82.7	81.5	78.4

0.01 Molar tetrapropylammonium iodide.

Ratio $I_2/N(C_3H_7)_4I$ .....	0	1	2
Molecular conductivity...	73.5	64.7	61.4

# IONISATION IN NON-AQUEOUS SOLVENTS. PART I. 1603

Polyiodides were found to be precipitated from the methylalcohol solution of the tetrapropylammonium salt when larger quantities of iodine were added.

## Ethyl Alcohol.

### 0.05 Molar potassium iodide.

Ratio $I_2/KI$ .....	0	0.5	1	2	3	4	7
Molecular conductivity...	22.2	27.8	32.8	31.7	31.5	30.1	28.9

### 0.01 Molar potassium iodide.

Ratio $I_2/KI$ .....	0	0.5	1	2	3	4	7
Molecular conductivity...	29.6	34.0	38.3	38.6	37.8	37.2	36.2

From ethyl alcoholic solutions of the substituted ammonium iodides, polyiodides were precipitated on the addition of relatively small quantities of iodine, and comparative measurements could not therefore be made in these cases.

## Methyl Acetate.

### 0.01 Molar potassium iodide.

Ratio $I_2/KI$ .....	0	0.5	1	2	3	4	7
Molecular conductivity...	1.15	9.85	16.2	22.4	24.6	25.7	27.3

### Ethyl Acetate (moist).

### 0.01 Molar potassium iodide.

Ratio $I_2/KI$ .....	0	0.5	1	2	3	4	7
Molecular conductivity...	0.38	5.45	9.0	13.7	16.0	17.0	18.4

In order to obtain a 0.01 molar solution of the iodide, it was necessary to add a little water to the ethyl acetate, and the solvent used in this series of measurements contained about 1.3 volumes per cent. of water.

## Ethyl Acetate (saturated with water at 18°).

### 0.1 Molar potassium iodide.

Ratio $I_2/KI$ .....	0	1	2	3	4	5
Molecular conductivity .....	—	15.7	22.7	24.4	25.9	26.7

These measurements were made because of the fact that experiments relating to the chemical dissociation of the polyiodides in ethyl acetate solution were carried out, as will be seen later, with this concentration, and with solutions saturated with water.



*Benzonitrile.*

0.01 Molar tetraethylammonium iodide.

Ratio $I_2/N(C_2H_5)_4I$ .....	0	0.5	1	2	3
Molecular conductivity.....	31.1	32.9	35.0	34.3	33.6

*Nitromethane.*

0.01 Molar tetraethylammonium iodide.

Ratio $I_2/N(C_2H_5)_4I$ .....	0	0.5	1	2	3
Molecular conductivity.....	85.7	86.5	85.7	82.0	79.4

*Nitrobenzene.*

0.01 Molar potassium iodide.

Ratio $I_2/KI$ .....	0	1	2	3	4	7
Molecular conductivity.....	(19)	27.0	28.1	28.3	29.2	29.7

According to Euler (*Zeitsch. physikal. Chem.*, 1899, **28**, 622), the molecular conductivity of potassium iodide in nitrobenzene at concentrations of 0.001, 0.0005, and 0.00025 mol. per litre is 19, 19, and 19.5 respectively. According to these numbers,\* the molecular conductivity does not vary appreciably with the dilution, and therefore it may be assumed that 19 is the approximate value of the conductivity of the 0.01 molar iodine-free solution, which, of course, cannot be prepared by reason of the slight solubility of the salt.

*Acetic Acid.*

0.01 Molar potassium iodide.

Ratio $I_2/KI$ .....	0	1	2	3	4
Molecular conductivity...	—	2.08	3.05	3.6	3.05

Before entering into a discussion of the relationships which are exhibited by the foregoing data, reference may be made to the question of polyiodide formation in the various solvents. In the case of aqueous solutions, irrefutable evidence in favour of the existence of tri-iodides has been brought forward, and various facts point to the formation of higher polyiodides as the concentration of the solution increases. From the value of the constant for the equilibrium  $KI_3 \rightleftharpoons KI + I_2$  in aqueous solution, it can be shown that in a 0.1 molar solution of the tri-iodide this would be dissociated to the extent of about 10 per cent., and in 0.01 molar solution to about 35 per cent. The chemical dissociation of the higher polyiodides is very much greater, and on this account water represents a solvent which is relatively unfavourable to the formation of perhalogen compounds.

On the other hand, nitrobenzene is a solvent in which chemical dissociation of the polyiodides takes place to only a very limited extent, and on this account it has been possible to show the formation of definite compounds of the types  $MI_3$ ,  $MI_5$ ,  $MI_7$ , and  $MI_9$  in such solutions. The similarity in the solubility relationships (Dawson, *Trans.*, 1904, 85, 467) exhibited by other organic solvents in comparison with nitrobenzene supports the view that more or less stable polyiodides of the same kind are also formed in these solutions. For an actual proof of this it would be necessary to carry out series of measurements similar to those which have already been made in the case of nitrobenzene. Such experiments would afford information relative to the degree of stability of the polyiodides in the different solvents; but this problem was obviously beyond the scope of the present investigation, and on this account it was considered sufficient to examine the polyiodide formation in one only of the solvents other than nitrobenzene. Ethyl acetate was chosen for this purpose, partly in consequence of the remarkable increase which takes place in the conductivity as the relative proportion of iodine to iodide increases, and also because of the fact that this solvent is only partly miscible with water.

The method employed in the test for dissolved polyiodides was essentially the same as that already described in the investigation of nitrobenzene solutions (*Trans.*, 1908, 93, 1312). Potassium iodide and iodine were dissolved in ethyl acetate, previously saturated with water at  $18^\circ$ , the quantities of substance weighed out being such as to give 0.1 molar solutions of the composition  $(KI + I_2)$ ,  $(KI + 2I_2)$ ,  $(KI + 3I_2)$ , and  $(KI + 4I_2)$ . Portions of each of these solutions were then carefully shaken up at  $18^\circ$  with appropriate quantities of a solution containing the equilibrium amount of potassium iodide dissolved in water, which had been previously saturated with ethyl acetate at the same temperature.

When the shaking, incidental to the attainment of equilibrium between the two layers of liquid, is carried out in such a way that very small drops are not formed, there is no difficulty attaching to the distribution experiments in the case of the first three solutions. The solution of the composition 0.1 molar  $(KI + 4I_2)$  is, however, very nearly of the same density as the corresponding aqueous solution, and although separation takes place after the preliminary agitations, it was found that the two layers soon coalesced to form a homogeneous liquid. On this account, the experiments with the  $(KI + 4I_2)$  solution were not carried to completion. A similar coalescence was observed later in the case of the ethyl acetate solution containing iodine and potassium iodide in the ratio  $3I_2:KI$ . After about a fortnight, during which this

solution was allowed to remain in contact with its equilibrium aqueous solution, the two liquids, although originally of appreciably different density, were found to have given rise to a single solution. This rather curious phenomenon has not been further investigated as yet.

From the iodide and total iodine concentrations of the equilibrium aqueous solutions, it is possible to calculate the concentration of free iodine by means of the constant for the equilibrium  $\text{KI}_3 \rightleftharpoons \text{KI} + \text{I}_2$ . At  $18^\circ$ ,  $K = [\text{KI}][\text{I}_2]/[\text{KI}_3]$  is equal to 0.00115. It seems likely, however, that the presence of ethyl acetate in the aqueous solution will alter to some extent the value of this constant, and for this reason the free iodine concentration can only be estimated approximately.

The following table contains the data:

Composition of ethyl acetate solutions.	Composition of aqueous solutions in equilibrium with the ethyl acetate solutions.		
	Mols. KI per litre.	Mols. iodine per litre.	Mols. free iodine per litre.
0.1 mol. $(\text{KI} + \text{I}_2)$ .....	2.3	0.00010	0.00000005
0.1 " $(\text{KI} + 2\text{I}_2)$ .....	0.025	0.0015	0.00007
0.1 " $(\text{KI} + 3\text{I}_2)$ .....	0.008	0.0008	0.00011

On account of the uncertainty attaching to the iodine distribution ratio, the question of polyiodide formation is most conveniently examined by reference to the data in the fourth column of the table. If the order of magnitude of the iodine distribution ratio (about 200) is taken into consideration, it is evident that these numbers indicate that the first ethyl acetate solution contains a very stable tri-iodide, and that the other two contain respectively penta- and hepta-iodide, which are chemically dissociated to but a comparatively small extent.

In thus favouring the formation of polyiodides, ethyl acetate is very similar to nitrobenzene, and it is probable that compounds of the same series are formed in both solvents. As already mentioned, there are also good grounds for the assumption that similar polyhalogen compounds are formed in the other solvents which have been examined in regard to their electrical conductivity.

Returning to the consideration of the electrical conductivities of the iodide and polyiodide solutions, it may be noticed that in nearly every instance the conductivity increases on passing from the iodide to the tri-iodide. In certain cases, for example, the 0.05 molar solutions in ethyl alcohol, this increase is followed by a decrease of conductivity on passing to the higher polyiodides, whilst in others, such as the methyl and ethyl acetate solutions, the higher polyiodides conduct very much better than the tri-iodide.

The relationships involved are clearly shown by means of the curves which are obtained when the molecular conductivity is plotted as a function of the iodine concentration. For two typical cases they are sufficiently evident from the following table, in which the conductivities of the various polyiodide solutions are expressed in terms of the conductivity of the iodide solution which is made equal to unity.

*Relative Conductivities of 0.05 Molar Solutions in Ethyl Alcohol.*

KI.	KI <sub>3</sub> .	KI <sub>5</sub> .	KI <sub>7</sub> .	KI <sub>9</sub> .
1	1.48	1.43	1.42	1.36

*Relative Conductivities of 0.01 Molar Solutions in Moist Ethyl Acetate.*

KI.	KI <sub>3</sub> .	KI <sub>5</sub> .	KI <sub>7</sub> .	KI <sub>9</sub> .
1	28.7	36.0	42.1	44.7*

\* It is probably safe to infer that these ratios would be still greater in the case of anhydrous ethyl acetate.

The variations in conductivity which are found in these cases may be conveniently compared with those exhibited by aqueous solutions. On the addition of successive quantities of iodine to an aqueous solution of potassium iodide, the conductivity decreases in a regular manner. Since the iodide and tri-iodide, which are alone involved in the case of the aqueous solution, are equally ionised (Dawson, Trans., 1901, **79**, 238; Burgess and Chapman, Trans., 1904, **85**, 1305; Bray and MacKay, *J. Amer. Chem. Soc.*, 1910, **32**, 914), the observed fall in conducting power is due to the smaller mobility of the tri-iodide as compared with that of the iodide ion. As a result of this diminished mobility, the conductivity of the tri-iodide is about 25 per cent. smaller than that of the iodide.

A similar influence of increasing anionic complexity may be expected in non-aqueous solvents, although the magnitude of the effect may be somewhat different. In contrast with aqueous solutions, however, the conductivity of potassium tri-iodide in the non-aqueous solutions is generally greater, and in certain cases enormously greater, than that of the iodide. In methyl and ethyl acetates, the conductivity of the higher polyiodides is also very much larger than that of the tri-iodide.

There can be little doubt\* that the observed variations in

\* The fact that liquid iodine yields good conducting solutions when potassium iodide is dissolved in it (Lewis and Wheeler, *Zeitsch. physikal. Chem.*, 1906, **56**, 179) cannot have much influence on the conductivities with which we are concerned.

conductivity are due to differences in the extent to which the various electrolytes are ionised, and it is evident that in certain solvents these differences are remarkably large.

The proof that the polyiodides of the alkali metals are ionised to a much greater extent than the simple iodides in certain solvents, is of particular interest in connexion with Walden's idea of a "normal" electrolyte (*Zeitsch. physikal. Chem.*, 1906, 54, 129). This conception is in agreement with the fact that, in a given solvent, different binary salts of the type  $M'X'$  are ionised to nearly the same extent when the solutions are dilute. At moderate dilutions differences are exhibited by the individual salts, but these are very small in comparison with the vast differences in the extent to which the alkali iodides and the corresponding polyiodides are ionised in solvents such as methyl and ethyl acetate. The simple iodides, when dissolved in these esters, behave like weak electrolytes in comparison with the polyiodides. The corresponding differences between the iodides and polyiodides of the tetra-substituted ammonium bases are probably much smaller, as in the case of nitrobenzene solutions (Dawson and Jackson, *Trans.*, 1908, 93, 2071) which have been examined previously. For this solvent, the conductivity data indicate that the polyiodides of the alkali metals are normally ionised, and if this is true for other solvents, as seems very probable, it follows that the ionisation of the alkali metal iodides is abnormally small in the case of certain non-aqueous solvents.

The choice of tetraethylammonium iodide as a "normal" electrolyte by Walden was based largely on solubility considerations. Apart from the difficult solubility, there would appear to be no particular reason for the selection of this in preference to an alkali metal iodide. The observations recorded in this paper indicate, however, that these are abnormally weak electrolytes when dissolved in certain liquid media, and any attempt to utilise them for comparison of the ionising powers of different solvents would therefore lead to discrepant results.

As to the cause of the difference between the ionisation of the iodides and that of the polyiodides, the various theories which have been put forward to account for the relative ionising powers of different solvents offer no explanation. This is necessarily the case in so far as such theories involve the consideration of the properties of the solvent alone. When, however, such large differences in ionisation are exhibited by closely related electrolytes in one and the same medium, it is clear that the character of the medium is of itself insufficient to account for the observed facts,

#### REMARKS ON 3:5-DINITROQUINOL

and some regard must be paid to the nature of the dissolved electrolyte

In a recent paper (Turner, this vol., p. 880) evidence has been brought forward in favour of a connexion between electrical conductivity and molecular association. From a comparison of the molecular complexities and the electrical conductivities of a large number of halogen compounds, it appears that molecular association can only be exhibited by those substances which are electrically active. Salts, which in solvents of low dielectric constant are associated, exhibit electrolytic dissociation when dissolved in liquids of high dielectric constant. The formation of the polyiodides may be regarded as an association phenomenon, and the greater conductivity of these as compared with the simple iodides of the alkali metals is possibly a consequence of the association of iodine atoms which is involved in the formation of the complex polyiodides. Such association or formation of complexes would appear to be intimately bound up with the phenomenon of ionisation, for, generally speaking, the ionising solvents are those which show a pronounced tendency to form complex compounds with substances which are dissolved in them.

PHYSICAL CHEMISTRY LABORATORY,  
THE UNIVERSITY, LEEDS.

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#### CLXXXII.—*Salts of 3:5-Dinitroquinol.*

By WILLIAM BATLISS SHAW.

ALTHOUGH the salts of the mono-, di-, and tri-nitrophenols have attracted considerable attention during the last few years, the metallic derivatives of the nitrodihydroxybenzenes have remained practically unknown.

The author has prepared a considerable number of the alkali-metal salts of mono- and di-nitrohydroxybenzenes.

In the present communication those of 3:5-dinitroquinol are described, and the author hopes shortly to publish details of the corresponding derivatives of catechol and resorcinol.

Dinitroquinol was first obtained by Strecker (*Annalen*, 1861, 118, 292) by the action of nitric acid on arbutin. Nietzki (*Ber.*, 1878, 11, 469; *Annalen*, 1882, 215, 142) obtained it by direct nitration of quinol diacetate. He prepared the neutral barium salt, but did not succeed in isolating any of the other salts owing to their great solubility in water.

It has, however, been found possible to obtain the alkali-metal salts of this substance in a very fair state of purity by the addition of an alcoholic solution of the metallic hydroxide to an ethereal solution of the nitro-compound. The salt is immediately precipitated, and is then collected and dried.

The analyses have been carried out by evaporating the salts with, first, a mixture of sulphuric and nitric acids, and then with sulphuric acid alone in a platinum crucible, the metal being thus determined as sulphate.

#### EXPERIMENTAL.

##### *Preparation of 3:5-Dinitroquinol.*

The method adopted was a modified form of Nietzki's process (*loc. cit.*).

One hundred grams of quinol were heated with 250 c.c. of acetic anhydride for about an hour in an oil-bath, the temperature being maintained between 130° and 140° (Hesse, *Annalen*, 1880, 200, 244). The liquid was allowed to cool, and then slowly poured, with constant stirring, into a large volume of cold water, when quinol diacetate, being quite insoluble, separated out in colourless plates. The whole was kept for an hour or so in order to allow the excess of acetic anhydride to become hydrolysed, and the crystals were then collected and dried in the air. The yield was practically quantitative.

The quinol diacetate so obtained was directly nitrated according to Nietzki's directions (*loc. cit.*).

Nietzki's original method of hydrolysis consisted in dissolving the dinitroquinol diacetate in dilute sodium hydroxide, acidifying the violet solution so produced, and extracting the dinitroquinol with ether.

The following procedure was found to be much more expeditious. The dinitroquinol, washed as free as possible from nitric acid, was placed in an evaporating dish and covered with alcohol, a few c.c. of dilute hydrochloric acid being added to the mixture. On evaporating on the water-bath with occasional stirring, the acetyl groups were rapidly eliminated as acetic ester.

The process was repeated to ensure complete hydrolysis, although one evaporation was usually found to suffice.

The dinitroquinol obtained in this way was almost always pure yellow, but sometimes possessed a reddish tinge, probably due to the presence of some impurity. One recrystallisation from boiling water gave a substance which was practically pure.

The recrystallised dinitroquinol after being dried in a desiccator was pale yellow, and melted at  $135^{\circ}$ . It was employed for the preparation of the salts without further purification.

*Preparation of the Salts.*

One of the barium salts has already been described by Nietzki (*Annalen*, 1882, 215, 144; *Ber.*, 1878, 11, 470), who prepared it by the addition of baryta water to an aqueous solution of the nitro-compound.

He states that it crystallises in black needles, which resemble potassium permanganate. He found that it dissolved in an aqueous solution of the free nitro-compound with the formation of the yellow acid salt, which, however, he was not able to obtain in a pure form.

These two salts have now been prepared by slightly different methods in a state of purity.

*Neutral Barium Salt,  $C_6H_2(NO_2)_2O_2Ba, H_2O$ .*

Dinitroquinol was dissolved in alcohol, and baryta water was cautiously added until the liquid was very faintly alkaline. The dark-coloured precipitate was collected, washed well with alcohol and ether, and dried in a water-oven for several hours.

The substance when dry was a dark blue, crystalline solid, and was fairly explosive. It had no resemblance to the substance described by Nietzki.

Two separately prepared specimens were analysed:

- (i) 0.1942 gave 0.1276  $BaSO_4$ .  $Ba = 38.64$ .
- (ii) 0.2227 „ 0.1472  $BaSO_4$ .  $Ba = 38.86$ .

$C_6H_2O_6N_2Ba, H_2O$  requires  $Ba = 38.81$  per cent.

The substance thus contains a molecule of water, and this it has not been found possible to remove, either by moderate heating or by keeping over sulphuric acid in a vacuum.

Nietzki does not give any particulars of his method of drying, but it is not easy to see how he obtained the salt in an anhydrous state.

*Acid Barium Salt,  $[HO \cdot C_6H_2(NO_2)_2 \cdot O]_2Ba, 2H_2O$ .*

This was prepared by boiling an aqueous solution of dinitroquinol with barium carbonate for about a quarter of an hour. The liquid was filtered hot, and, on cooling, deposited dark red crystals, which were collected, and dried in the water-oven.

Found:  $Ba = 24.15$ .

$C_{12}H_6O_{12}N_4Ba, 2H_2O$  requires  $Ba = 23.99$  per cent.



*Neutral Lithium Salt,  $C_6H_2(NO_2)_2(OLi)_2 \cdot H_2O$* 

Dinitroquinol was dissolved in alcohol, and an aqueous solution of lithium hydroxide was added until the liquid was just alkaline. A little ether was then added, and the precipitate was collected, washed with alcohol and ether, and dried in the water-oven. The substance was dark violet.

Found: Li=6.00.

$C_6H_2O_6N_2Li_2 \cdot H_2O$  requires Li=6.09 per cent.

*Acid Lithium Salt,  $HO \cdot C_6H_2(NO_2)_2 \cdot OLi$* 

Dinitroquinol was dissolved in ether, and methyl-alcoholic lithium hydroxide added until the red liquid just began to acquire a violet colour. The red precipitate was collected, washed with ether, and dried.

Found: Li=3.36.

$C_6H_3O_6N_2Li$  requires Li=3.40 per cent.

*Acid Sodium Salt,  $C_6H_2(NO_2)_2(ONa)_2$* 

Dinitroquinol was dissolved in the smallest possible quantity of alcohol, and largely diluted with ether. Dilute alcoholic sodium hydroxide was carefully added until the brown liquid showed a blue tinge. The precipitate was collected, washed with ether, and dried. It formed a brown solid.

Found: Na=10.68.

$C_6H_3O_6N_2Na$  requires Na=10.36 per cent.

*Neutral Sodium Salt,  $HO \cdot C_6H_2(NO_2)_2 \cdot ONa$* 

Dinitroquinol was dissolved, and treated as above, until a very slight excess of alkali was present. The precipitate was collected, washed, and dried as usual. The substance was a blue solid.

Found: Na=18.48.

$C_6H_2O_6N_2Na_2$  requires Na=18.85 per cent.

*Acid Potassium Salt,  $HO \cdot C_6H_2(NO_2)_2 \cdot OK$* 

Dinitroquinol was dissolved in alcohol, some ether was added, and then dilute alcoholic potassium hydroxide until the red liquid acquired a violet tinge. The precipitate was collected, washed, and dried. The substance was a brown solid.

Found: K=16.23.

$C_6H_3O_6N_2K$  requires K=16.39 per cent.

*Neutral Potassium Salt,  $C_6H_2(NO_2)_2(OK)_2 \cdot H_2O$ .*

The method of preparation was the same as in the case of the sodium salt, using alcoholic potassium hydroxide in place of alcoholic sodium hydroxide. The substance was dark violet.

Found:  $K = 26.22$ .

$C_6H_2O_6N_2K_2 \cdot H_2O$  requires  $K = 26.54$  per cent.

*Ammonium Salts.*

It has not been possible to obtain these in a state of purity owing to the readiness with which they lose ammonia.

*3:5-Dinitroquinol 1-Monomethyl Ether.*

This compound has been obtained by the following method.

Five grams of dinitroquinol were dissolved in half a litre of warm water, and the solution rendered alkaline with sodium hydroxide. A roughly estimated excess of methyl sulphate was then added, and the liquid maintained at about  $60^\circ$ , with continual shaking, until the violet solution became pale yellow. The liquid was then filtered hot, and allowed to cool, when the monomethyl ether separated in fine crystals, which did not need further purification.

Dinitroquinol monomethyl ether has already been described by Weselsky and Benedikt (*Monatsh.*, 1881, 2, 370), who prepared it by the direct nitration of quinol monomethyl ether.

According to them it melts at  $102^\circ$ , but two carefully purified specimens prepared as above both melted at  $97^\circ$ . It is most probable that the methoxyl group occupies the meta-position with respect to the two nitro-groups, for the analogous dinitroguaiacol is

known to have the formula  $\begin{array}{c} \text{NO}_2 \text{ OH} \\ \diagdown \quad \diagup \\ \text{C}_6\text{H}_3 \\ \diagup \quad \diagdown \\ \text{NO}_2 \quad \text{OMe} \end{array}$  (Grimaux and Lefèvre,

*Bull. Soc. chim.*, 1891, [iii], 5, 418).

*Salts of 3:5-Dinitroquinol 1-Monomethyl Ether.*

*Lithium Salt,  $MeO \cdot C_6H_2(NO_2)_2 \cdot OLi$ .*—The monomethyl ether was dissolved in warm chloroform, and a methyl-alcoholic solution of lithium hydroxide cautiously added until precipitation of the salt was complete. The precipitate was collected, washed with chloroform and ether, and dried.

Found:  $Li = 3.30$ .

$C_7H_5O_6N_2Li$  requires  $Li = 3.18$  per cent.

*Sodium Salt,  $MeO \cdot C_6H_2(NO_2)_2 \cdot ONa$ .*—The procedure was the

same as in the case of the lithium salt, alcoholic sodium hydroxide being substituted for methyl-alcoholic lithium hydroxide.

Found: Na=10.5.

$C_7H_5O_6N_2Li$  requires Na=9.74 per cent.

*Potassium Salt*,  $MeO \cdot C_6H_2(NO_2)_2 \cdot OK$ .—This salt has been described by Weselsky and Benedikt (*loc. cit.*), who state that dinitroquinol monomethyl ether is soluble in warm potassium hydroxide, and that on cooling green crystals of the potassium salt are formed. No analysis or further particulars are given. This salt has been prepared in the following way.

The monomethyl ether was dissolved in ether, and dilute alcoholic potassium hydroxide added until precipitation was complete. The precipitate was collected, washed with ether, and dried in the water-oven:

0.1368 gave 0.0478  $K_2SO_4$ . K=15.66.

$C_7H_5O_6N_2K$  requires K=15.47 per cent.

The salt is a bright crimson solid, which has no resemblance whatever to the substance described by Weselsky and Benedikt.

*Ammonium Salt*.—It has not been possible to prepare this salt in a state of purity, owing to the readiness with which it evolves ammonia.

The corresponding caesium and rubidium salts of the above compounds have been prepared, but have not yet been analysed, owing to the difficulty of determining accurately the percentage of these metals in organic compounds.

The colours of the salts present some features of interest.

The neutral salts have in every case the darkest colours, the sodium and barium salts being blue, and the rest violet. The acid salts are dark red, and the ether salts bright red.

The colour deepens progressively from lithium to caesium, but the barium salts are paler in colour than those of lithium. The ammonium salts have been obtained, although not in a state of purity, and appear to be intermediate in colour between those of barium and lithium. This is noteworthy since, crystallographically, ammonium is well known to stand near to rubidium.

In conclusion, I have to express my thanks to Professor E. von Meyer and Dr. W. König, of the Technische Hochschule, Dresden, for the kind interest they have taken in this work, and the many helpful suggestions they have made.

CLXXXIII.—2:2'-*Dibromodiphenyl* and 2:2'-*Dichlorodiphenyl*.

By JAMES JOHNSTON DOBBIE, JOHN JACOB FOX, and  
ARTHUR JOSIAH HOFFMEISTER GAUGE.

IN the course of an investigation having for its object the preparation of diphenylene (this vol., p. 683), it was necessary to obtain 2:2'-*dibromodiphenyl*, a substance hitherto unknown. Treatment of the tetrazo-derivative of 2:2'-diaminodiphenyl with cuprous bromide, as in the ordinary Sandmeyer reaction, suggested itself as a convenient method of preparation. This procedure ultimately proved successful, but unexpected difficulties arose in the first experiments, and very little dibromodiphenyl was formed. With the object of ascertaining the most suitable conditions for the reaction, the behaviour of cuprous bromide towards diphenyl-tetrazonium bromide under various conditions was investigated. Täuber had found that potassium sulphide reacted with diphenyl-tetrazonium chloride solutions, yielding carbazole (*Ber.*, 1893, **26**, 1703). This same substance had been obtained by v. Niementowski (*Ber.*, 1901, **36**, 3329), who made use of copper powder in an attempt to prepare dichlorodiphenyl. Mascarelli had also noticed that the main product of the reaction between diphenyltetrazonium chloride and potassium iodide was carbazole (*Gazzetta*, 1908, **38**, ii, 619), the di-iododiphenyl which was his aim being formed in small amount only. It is clear, therefore, that cuprous chloride and certain other reducing substances act on diphenyltetrazonium solutions mainly to produce the very stable substance carbazole.

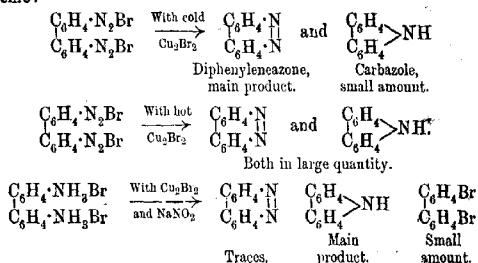
Cuprous bromide behaves in the same way as cuprous chloride, but at least two other products besides carbazole are formed simultaneously, namely, 2:2'-dibromodiphenyl and diphenyleneazone,



When a solution of cuprous bromide dissolved in hydrobromic acid is poured into a cold solution of diphenyltetrazonium bromide, diphenyleneazone is the main product of the reaction, very little carbazole or dibromodiphenyl being formed. If, on the other hand, diphenyltetrazonium bromide is poured into a hot solution of cuprous bromide, carbazole is formed to a much greater extent, and the amount of diphenyleneazone is diminished. In this case also, very little dibromodiphenyl is produced. A much better yield of the latter substance with a little diphenyleneazone and a con-

siderable proportion of carbazole is obtained when 2:2'-diaminodiphenyl is dissolved in a hot solution of cuprous bromide in concentrated hydrobromic acid, and treated with sodium nitrite. The amount of 2:2'-dibromodiphenyl isolated from the product of the reaction rarely, however, exceeds 8 to 10 per cent. of the theoretical quantity.

In a study of the Sandmeyer reaction as applied to the formation of *o*-chlorotoluene, Erdmann (*Annalen*, 1893, 272, 141) drew the conclusion that Sandmeyer's method of dissolving the base in a solution of the cuprous salt and halogen acid, and then diazotizing, leads to a diminished yield of the required halogen derivative as compared with the yield obtained when the diazonium solution is poured into the solution of the cuprous salt. In the present instance the reverse is the case; Sandmeyer's method gives an appreciable amount of dibromodiphenyl, whereas Erdmann's produces mainly carbazole and diphenyleneazone, with only traces of dibromodiphenyl. The reactions which take place between diphenyltetrazonium bromide and cuprous bromide under the various conditions referred to may be represented by the following scheme:



In an attempt to prepare dibromodiphenyl by the action of alcohol on diphenyltetrazonium perbromide, only traces of dibromodiphenyl were obtained, carbazole being the main product of the reaction.

2:2'-Dibromodiphenyl can also be obtained from 2:2'-dibromo-4:4'-diaminodiphenyl by elimination of the amino-groups, both methods giving a product melting at 81°. As already shown in our previous paper, 2:2'-dibromodiphenyl reacts slowly with sodium, yielding diphenylene; mixed with methylene dibromide and acted on by sodium, it yields fluorene.

In order to complete the series of diortho-halogen derivatives of diphenyl, 2:2'-dichlorodiphenyl was prepared by a method similar to that used in the preparation of 2:2'-dibromodiphenyl. The yield of this substance was smaller than that of the correspond-

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ing bromo-derivative, carbazole being again the main product. 2:2'-Dichlorodiphenyl crystallises from light petroleum in colourless prisms, melting at 59°. Both halogen derivatives are very stable towards oxidising agents, being scarcely, if at all, attacked, even by chromic acid mixture.

### EXPERIMENTAL.

*Formation of Diphenyleneazone.*—2:2'-Diaminodiphenyl was dissolved in excess of hydrobromic acid, and diluted with water until the solution contained approximately 3 per cent. of the base. The solution was cooled to 0°, and diazotised with sodium nitrite. To the tetrazonium solution so formed, cuprous bromide, dissolved in hydrobromic acid (40 grams of  $\text{Cu}_2\text{Br}_2$  to 50 c.c. of acid, D 1.49), was slowly added with stirring, the solution being kept cool by means of ice. Each addition of cuprous bromide was followed by a vigorous evolution of gas and formation of a bluish-black mass enclosing nitric oxide. The products of the reaction were heated on a water-bath for an hour, and the liquid then filtered from the solid matter (A). The filtrate was evaporated to small volume, and on treatment with excess of ammonia a large amount of almost pure diphenyleneazone was precipitated. The solid (A) was boiled with 15 per cent. hydrochloric acid, the acid liquid filtered from undissolved solid matter (B), and the filtrate treated with excess of ammonia, which precipitated a further quantity of slightly impure diphenyleneazone. After one crystallisation from alcohol, the diphenyleneazone was obtained pure in the form of long, greenish-yellow prisms, melting at 155°. The yield was good, 11 grams of pure material being obtained from 20 grams of 2:2'-diaminodiphenyl. The identity of this substance with the diphenyleneazone obtained by Täuber by the action of sodium amalgam on 2:2'-dinitrodiphenyl (*Ber.*, 1891, **24**, 3081), and by Ullmann and Dieterle from diphenyleneazone oxide (*Ber.*, 1904, **37**, 23), was proved by the melting point and by analysis of the base (Found, N=15.7. Calc., N=15.6 per cent.) and of the platinum salt. (Found, Pt=25.1. Calc., Pt=25.0 per cent.)

It is noteworthy that the formation of diphenyleneazone by the above process is accompanied by evolution of nitric oxide.

The solid (B) was found to contain carbazole, which was extracted by successive treatment with alcohol, ether, benzene, and carbon tetrachloride. These solutions were boiled with animal charcoal, and concentrated, when crystals were deposited, from which pure carbazole was ultimately obtained. The first crops of carbazole crystals were mixed with a very small quantity of dibromodiphenyl.

Attempts to increase the yields of dibromodiphenyl were next made by modifying the method described above in various directions. The diphenyltetrazonium bromide solution was poured into a hot solution of cuprous bromide dissolved in hydrobromic acid. The black, tarry solid which formed yielded a fair amount of carbazole and of diphenyleneazone, but only traces of dibromodiphenyl. By this method the amount of diphenyleneazone was diminished, and that of the carbazole increased.

*Preparation of 2:2'-Dibromodiphenyl.*—When 2:2'-diaminodiphenyl hydrobromide is diazotised in the presence of cuprous bromide, dibromodiphenyl is formed, together with other products. Thirty-six grams of cuprous bromide were dissolved in 90 c.c. of hydrobromic acid (D 1.49), and 20 grams of 2:2'-diaminodiphenyl added. The liquid was heated on a water-bath, and small quantities of hot water added from time to time until all the solid was dissolved. Sixteen grams of sodium nitrite in 50 c.c. of water were added to the hot solution of the base drop by drop, with vigorous stirring after the addition of each drop, the heating being continued during the addition of the nitrite solution. When all the nitrite had been added, the liquid was heated on a water-bath for an hour, cooled, and diluted with water. The dark soft solid which separated was collected, washed with water, and digested with ether several times. A considerable amount of solid matter containing carbazole remained undissolved in the ether. The undissolved matter also contained some copper compound, but this was not further investigated. A very small amount of diphenyleneazone was obtained from the aqueous filtrate from the soft solid. The ethereal solution, which contained almost all the dibromodiphenyl, was boiled with animal charcoal, filtered, and evaporated to a syrupy consistency. The syrupy residue was distilled in a current of steam, in which the dibromodiphenyl, together with a little carbazole, passed over. This method of separation is slow, but, so far, is the only one by which we have been able to obtain dibromodiphenyl free from coloured impurities. The distillate was extracted with ether, and the crystalline residue obtained by evaporation of the ethereal solution, dissolved in light petroleum (boiling below 60°), and allowed to crystallise. A small quantity of carbazole first separated, and was removed by filtration. Dibromodiphenyl crystallised from the filtrate in long, hard, colourless prisms or in feathery tufts of needles, which melted at 81° after recrystallisation from 90 per cent. alcohol. The yield is about 15 per cent. of the weight of the base employed.

2:2'-Dibromodiphenyl is readily soluble in the usual organic solvents. It is very stable towards oxidising agents; after heating

with a mixture of chromic acid and diluted sulphuric acid for five hours practically the whole of the substance was recovered unchanged. Advantage may be taken of this fact to remove traces of impurities:

0.1346 gave 0.2262  $\text{CO}_2$  and 0.0323  $\text{H}_2\text{O}$ .  $\text{C}=45.9$ ;  $\text{H}=2.65$ .

0.1226 „ 0.1482  $\text{AgBr}$ .  $\text{Br}=51.4$ .

$\text{C}_{12}\text{H}_8\text{Br}_2$  requires  $\text{C}=46.2$ ;  $\text{H}=2.6$ ;  $\text{Br}=51.3$  per cent.

The constitution of dibromodiphenyl follows from its preparation from 2:2'-diaminodiphenyl.

2:2'-Dibromodiphenyl can also be prepared from 2:2'-dibromo-4:4'-diaminodiphenyl (*mm'*-dibromobenzidine), a substance which was obtained by Gabriel from *m*-bromonitrobenzene (*Ber.*, 1876, 9, 1405). For the preparation of dibromodiphenyl, the hydrochloride which is obtained from *mm'*-dibromohydrazobenzene may be used directly after drying. The amino-groups can be removed by means of ethyl nitrite and alcohol in the usual way. The resulting alcoholic solution is evaporated to dryness, and the residue distilled in steam, whereby an impure dibromodiphenyl is obtained. After purification, the substance prepared in this way melted at  $81^\circ$ , and no alteration in the melting point was observed when it was mixed with the dibromodiphenyl prepared from 2:2'-diaminodiphenyl. As regards yield, the preparation from *mm'*-dibromobenzidine offers no advantage over the first method, and the final product requires several recrystallisations involving considerable loss of material before it is obtained quite pure.

An attempt to prepare 2:2'-dibromodiphenyl through a perbromide was made. 2:2'-Diaminodiphenyl was diazotised, and to the tetrazo-solution a mixture of bromine in hydrobromic acid was added. A bulky, yellow precipitate of the perbromide formed at once. This was collected, and boiled with absolute alcohol, the solution changing in colour through green and blue to brown. After removal of the alcohol a fair amount of diphenyleneazone was obtained, but only traces of halogen derivative.

*Preparation of 2:2'-Dichlorodiphenyl.*—2:2'-Diaminodiphenyl was dissolved in hydrochloric acid containing the calculated quantity of cuprous chloride. The solution was then heated, and treated with sodium nitrite, as in the preparation of 2:2'-dibromodiphenyl. The subsequent treatment of the soft, black solid was also similar. A large amount of carbazole was isolated from the reaction products, and a small quantity of dichlorodiphenyl was found in the ethereal solutions. After distillation in a current of steam a mixture of dichlorodiphenyl with a little carbazole was obtained, from which the pure dichlorodiphenyl was isolated by recrystallisation from light petroleum, in which carbazole is but sparingly soluble.



2:2'-Dichlorodiphenyl crystallises from light petroleum in nodular masses of colourless prisms, melting at  $59^{\circ}$ . It dissolves in the usual organic solvents, and is stable towards oxidising agents:

0.1134 gave 0.1428 AgCl.  $\text{Cl} = 31.2$ .

$\text{C}_{12}\text{H}_8\text{Cl}_2$  requires  $\text{Cl} = 31.8$  per cent.

An interesting synthesis of fluorene was effected by the action of sodium on a mixture of 2:2'-dibromodiphenyl and excess of methylene dibromide dissolved in ether. The crystalline residue remaining after evaporating off the ether contained unchanged dibromodiphenyl, which was removed by recrystallisation from alcohol and light petroleum. After recrystallisation several times from these solvents a small amount of almost pure fluorene was obtained, melting at  $115^{\circ}$ . The substance was further identified by the preparation of the characteristic brown picrate, melting at  $80^{\circ}$ .

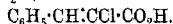
GOVERNMENT LABORATORY,  
LONDON.

#### CLXXXIV.—The $\beta$ -Chlorocinnamic Acids.

By THOMAS CAMPBELL JAMES.

THE  $\beta$ -chlorocinnamic acids have been previously studied by W. H. Perkin, jun. (Trans., 1885, **47**, 256), by Michael and Pendleton (*J. pr. Chem.*, 1889, [ii], **40**, 65), and by Mulliken (*Diss.*, Leipzig, 1890). Perkin found that when phosphorus pentachloride was added to ethyl benzoylacetate in phosphoryl chloride solution, a chlorocinnamic acid, melting at  $142^{\circ}$ , was obtained, which was supposed by him to be identical with the  $\alpha$ -chlorocinnamic acid, melting at  $138^{\circ}$ , previously prepared by Plochl (*Ber.*, 1882, **15**, 1945).

The application of the theory of stereoisomerism to unsaturated compounds indicated the possible existence of two  $\beta$ -chlorocinnamic acids,  $\text{C}_6\text{H}_5\cdot\text{CCl}:\text{CH}\cdot\text{CO}_2\text{H}$ , as well as two  $\alpha$ -acids,



The former were prepared by Michael and Pendleton (*loc. cit.*) by the addition of hydrogen chloride to phenylpropionic acid in acetic acid solution. They were separated by taking advantage of the great difference of solubility of their potassium salts in absolute alcohol. The acid obtained from the readily soluble salt melted at  $132.5^{\circ}$ , and was called  $\beta$ -chlorocinnamic acid, the other melting at  $142^{\circ}$ ,  $\beta$ -chloro*allo*cinnamic acid.

Mulliken showed that phenylpropionic acid combines with hydrogen chloride when it is heated with the fuming aqueous acid at 80–90° for three hours. By examining the action of heat on the two isomerides, he found that the acid melting at 142° was the more stable, and should therefore be called  $\beta$ -chlorocinnamic acid, the compound of lower melting point being the *allo*-acid.

In the present investigation the methods of preparation mentioned above have been examined, and the proportion in which the two isomerides are formed determined in each case. It has been found that the method of separation by means of barium salts applied in the case of the  $\alpha$ - and  $\beta$ -bromocinnamic acids (Sudborough and Thompson, *Trans.*, 1903, **83**, 666, 1153) and the  $\alpha$ -chlorocinnamic acids (Sudborough and James, *Trans.*, 1906, **89**, 105) is applicable in this case also. The action of sunlight on the two isomerides and the rates of elimination of hydrogen chloride have been examined, the results of these experiments taken in conjunction with the esterification constants (Sudborough and Roberts, *Trans.*, 1905, **87**, 1849) proving definitely that the acid melting at 132.5° is the *allo*-compound. Various derivatives of the acids have also been prepared.

#### EXPERIMENTAL.

##### *Separation of the $\beta$ -Chlorocinnamic Acids.*

Two grams of each acid were mixed and dissolved in water with the addition of aqueous ammonia, the total volume being 40 c.c. After neutralising the excess of ammonia with hydrochloric acid, 20 c.c. of a cold saturated solution of barium chloride were added, and the mixture allowed to remain for two hours. The precipitated barium salt was collected, and washed three times with small quantities of dilute barium chloride solution, after which it was treated with dilute hydrochloric acid. The filtrate containing the soluble barium salt was treated with concentrated hydrochloric acid, and the acids precipitated in each case were washed with dilute acid, dried, and weighed.

The sparingly soluble barium salt gave 2.06 grams of acid, which after recrystallisation melted at 142°. The soluble salt gave 1.92 grams of acid, melting at 131°. Total yield, 3.98 grams. The separation is therefore complete to within 4 per cent.

##### *Preparation of $\beta$ -Chlorocinnamic Acids.*

*Method 1. By the addition of hydrogen chloride in aqueous solution to phenylpropionic acid.*—Mulliken (*loc. cit.*) established the fact that at temperatures below 80° addition of hydrogen chloride to phenylpropionic acid takes place only very slowly.

Between 80° and 90° addition is complete in three hours, but considerable decomposition of the products takes place with the formation of acetophenone. No yields are mentioned, but the proportion of  $\beta$ -chloro-acid to its *allo*-isomeride is given at 61:39.

A series of experiments has confirmed Mulliken's results with regard to the conditions under which addition takes place. The total yield of  $\beta$ -chloro-acids is only about 40 per cent. of theory, of which rather more than one-half consists of the *allo*-isomeride.

A weighed amount of phenylpropionic acid was placed in a bomb tube, and treated with sufficient hydrogen chloride solution, saturated at 0°, to cover it. After sealing, the tube was heated in a water-bath kept at 80–90° for three hours. The product, which contained much oil, was washed with water, extracted with dilute alkali, and the solution, after neutralising, treated with barium chloride solution as described above. The results are given in the following table:

Experi- ment.	Phenyl- propionic acid. Grams.	Tempera- ture.	$\beta$ -Chloro- acid. Grams.	Yield per cent.	<i>allo</i> - Acid. Grams.	Yield per cent.	Total yield per cent.
1.	4	80–90°	0.80	16	0.95	19	35
2.	4	80–90°	0.85	17	1.25	25	42
3.	6	83°	1.50	20	1.60	21	41
		Average yields.....		18		22	40

*Method 2.* By the addition of hydrogen chloride to phenylpropionic acid in acetic acid solution at the ordinary temperature.—Michael and Pendleton (*loc. cit.*) state that the addition of hydrogen chloride to phenylpropionic acid in acetic acid solution produces the two isomerides, which after precipitating by adding to excess of water were separated by taking advantage of the difference of solubility of the potassium salts in absolute alcohol.

Ten grams of phenylpropionic acid were dissolved in 50 grams of glacial acetic acid, and dry hydrogen chloride passed in until the solution was saturated at 0°. The mixture was kept in a sealed bottle in the dark at the ordinary temperature. Preliminary experiments showed that it required six weeks to attain complete addition under these conditions.

*Experiment 1.*—After remaining for six weeks the mixture was poured into excess of water, the precipitate collected, dried, and weighed. Weight=10.1 grams (theory, 12.5 grams).

*Experiment 2.*—After six weeks the mixture was poured into an evaporating dish, and the solvent allowed to evaporate off in a fume-cupboard in a dark room. Weight of product=11.0 grams.

*Experiment 3.*—It was found that by heating the mixture to 50–60°, addition takes place in eight hours, little oil-formation

occurring. Five grams of acid dissolved in 50 grams of acetic acid under these conditions yielded 4.0 grams of mixed acids.

The products in each case were separated by the barium salt method with the following results:

Experiment.	Weight of crude mixture. Grams.	$\beta$ -Chloro-acid. Grams.	Yield per cent.	$\beta$ -Chloro- <i>allo</i> -acid. Grams.	Yield per cent.
1.	10.1	5.0	40.0	4.4	35.2
2.	11.0	5.1	41.0	5.6	44.8
3.	4.0	1.6	25.6	1.8	28.8

The products possessed the correct melting points after one recrystallisation from alcohol and water. The numbers indicate that in each case approximately equal amounts of the two isomerides are obtained.

*Method 3. By the action of phosphorus pentachloride on the esters of benzoylacetic acid.*—Perkin in his investigation of benzoylacetic acid and its derivatives (*loc. cit.*) obtained a chlorocinnamic acid, melting at  $142^{\circ}$ , by the action of phosphorus pentachloride on the ethyl ester. Mulliken repeated the experiment, and identified the acid with the  $\beta$ -chlorocinnamic acid obtained by method 1. He also showed that the oily by-product of the reaction contains acetophenone.

A series of experiments carried out with the methyl and ethyl esters shows that both acids are obtained during the reaction. The method of procedure was based on that of Perkin.

Ten grams of the ester were dissolved in 25 grams of phosphoryl chloride (or phosphorus trichloride), and the solution added gradually to 25 grams of phosphorus pentachloride in a distilling flask. When the evolution of hydrogen chloride had ceased, the flask was heated in a water-bath until the solid pentachloride had disappeared. The phosphoryl chloride was then distilled off under diminished pressure, and the residue, after cooling, poured into water. The product, which contained much oil, was dissolved in ether, and shaken several times with small amounts of dilute ammonia solution to extract the acids. The aqueous extracts, after neutralising with hydrochloric acid, were treated with barium chloride solution and worked up in the usual manner.

The ethereal solution, after extracting the acids, was dried, and the ether distilled off, leaving a yellow oil. That derived from the experiments with the ethyl ester was distilled. The first fraction (25 per cent.), collected at  $200$ – $220^{\circ}$ , contained only traces of chlorine, gave a phenylhydrazone, melting at  $105^{\circ}$ , and was therefore acetophenone. The second fraction (50 per cent.), collected at  $240$ – $275^{\circ}$ , boiled chiefly at  $260$ – $265^{\circ}$  (uncorr.). It contained

15.5 per cent. of chlorine, and is the ester of an unsaturated acid, probably  $\beta$ -chloroallocinamic acid. The remaining portion charred and decomposed on heating further.

*Experiment 1.*—Ten grams of ethyl benzoylacetate were dissolved in 25 grams of phosphoryl chloride, and added gradually to 25 grams of phosphorus pentachloride. After separation there were obtained:

$\beta$ -Chlorocinnamic acid .....	4.60 grams	or	51.0 per cent.
$\beta$ -Chloroallocinamic acid..	1.50 "	"	16.4 "
Oil .....	2.0 "	"	"
Total yield of acids.....			67.4 "

*Experiment 2.*—Same as No. 1.

$\beta$ -Chloro-acid.....	3.95 grams	or	44.0 per cent.
$\beta$ -Chloroallo-acid .....	1.75 "	"	19.4 "
Oil .....	3.0 "	"	"
Total yield of acids.....			63.4 "

*Experiment 3.*—Solvent, phosphorus trichloride; otherwise as in Nos. 1 and 2.

Crude product .....	7.20 grams		
$\beta$ -Chloro-acid.....	4.65 "	or	51.6 per cent.
$\beta$ -Chloroallo-acid .....	1.90 "	"	21.1 "
Total yield of acids.....			72.7 "

*Experiment 4.*—As in No. 3, but the benzoylacetate ester was distilled immediately before the experiment.

$\beta$ -Chloro-acid.....	3.90 grams	or	43.3 per cent.
$\beta$ -Chloroallo-acid .....	2.10 "	"	23.3 "
Total yield of acids .....			66.6 "
Average yield of $\beta$ -chlorocinnamic acid			
(4 experiments).			47.5 "
" " $\beta$ -Chloroallocinamic acid			20.0 "

An experiment conducted with the methyl ester gave an improved yield of  $\beta$ -chlorocinnamic acid, with an increased proportion of the allo-acid.

*Experiment 5.*—Ten grams of methyl benzoylacetate in 25 grams of phosphorus trichloride added to 25 grams of phosphorus pentachloride.

Crude product .....	9.2 grams		
$\beta$ -Chlorocinnamic acid.....	4.10 "	or	42.0 per cent.
$\beta$ -Chloroallocinamic acid..	3.75 "	"	38.0 "
Oil .....	1.0 "	"	"
Total yield of acids.....			80.0 "

*Transformation of  $\beta$ -Chloroallocinamic Acid into its Isomeride.*

Mulliken has shown that the acid melting at  $132.5^\circ$  is largely transformed into the acid of higher melting point when kept at a

temperature of  $150^{\circ}$  for five hours. A similar transformation occurs at the ordinary temperature under the influence of sunlight.

One gram of each acid was exposed to sunlight during two months. At the end of this time the point of fusion of the acid of higher melting point was unchanged, but that of the other fell to  $120^{\circ}$ . On separation by means of barium salts the latter gave 0.2 gram of  $\beta$ -chlorocinnamic acid, melting at  $142^{\circ}$ .

*Action of Potassium Hydroxide on  $\beta$ -Chlorocinnamic Acids.*

By remaining in contact with aqueous alkalis both acids lose hydrogen chloride and yield phenylpropionic acid.

*Experiment 1.*—Two grams of  $\beta$ -chlorocinnamic acid were warmed with 2.5 mols. of aqueous potassium hydroxide solution (10 per cent.) on a water-bath for two hours. On acidifying, 1.55 grams of phenylpropionic acid (m. p.  $136^{\circ}$ ) were obtained. Theory, 1.60 grams.

*Experiment 2.*—A similar experiment was carried out with  $\beta$ -chloroallicinnamic acid, the mixture being warmed for six hours.

1.35 Grams of phenylpropionic acid were obtained, and the odour of phenylacetylene was detected, indicating partial decomposition of the carboxylic grouping.

The rate of elimination of hydrogen chloride by potassium hydroxide has been determined kinetically.

*$\beta$ -Chlorocinnamic Acid.*—1/100 Gram-equivalent of the acid was dissolved in 2 equivalents of  $N/10$ -potassium hydroxide solution. Twenty-five c.c. of the resulting solution were titrated at intervals with standard sulphuric acid.

Temperature of bath  $15^{\circ}$ . Strength of acid used for titration, 0.05708*N*.

Time in hours.	C.c. acid required.	$x$ .	$k = 1/t \frac{x}{a(a-x)}$
0 0	21.90	—	—
42 5	20.50	1.40	0.0000734
113 5	18.30	3.30	0.0000713
185 5	16.95	4.95	0.0000702
305 5	14.80	7.10	0.0000717
324.0	13.60	8.30	0.0000726
	Mean.....		0.00007184

Calculated for normal solution  $k=0.0915$ .

*$\beta$ -Chloroallicinnamic Acid.*—Three grams of the acid were dissolved in 2 equivalents of  $N/5$ -potassium hydroxide. Twenty c.c. of the resulting solution were titrated at intervals with standard sulphuric acid.

Temperature of bath 15°. Strength of acid used for titration, 0.1042*N*.

Time in hours.	C.c. acid required.	<i>x</i> .	$k = 1/t \cdot \frac{x}{a(a-x)}$
0	19.76	—	—
24	19.36	0.40	—
144	18.85	0.91	0.0000169
336	17.95	1.81	0.0000152
432	17.60	2.16	0.0000144
504	17.30	2.46	0.0000143
768	16.60	3.16	0.0000125
	Mean.....		0.0000147

Calculated for normal solution  $k = 0.00282$ .

From these values it is seen that  $\beta$ -chlorocinnamic acid (m. p. 142°) loses hydrogen chloride about eleven times as rapidly as  $\beta$ -chloroalloeicinnamic acid (m. p. 132°).

#### *Derivatives of the $\beta$ -Chlorocinnamic Acids.*

##### *$\beta$ -Chlorocinnamic Acid.*

*Ethyl Ester*.—Eight grams of acid were dissolved in 40 grams of absolute alcohol, and dry hydrogen chloride passed in until a 10 per cent. solution was obtained. The solution was boiled for six hours, and then worked up in the usual manner. Yield of ester, 6 grams. Boiling point, 293° (corr.):

0.2149 gave 0.1478 AgCl. Cl=17.01.

$C_{11}H_{11}O_2Cl$  requires Cl=16.85 per cent.

*Amide*.—Colourless, crystalline needles, melting at 118°:

0.2002 required 11.17 c.c. *N*/10-AgNO<sub>3</sub>. Cl=19.78.

$C_9H_8ONCl$  requires Cl=19.50 per cent.

*Anilide*.—Colourless, crystalline needles, melting at 128°:

0.2180 required 8.55 c.c. *N*/10-AgNO<sub>3</sub>. Cl=13.90.

$C_{15}H_{12}ONCl$  requires Cl=13.77 per cent.

*p-Toluidide*.—Crystalline needles, melting at 122.5°:

0.2050 required 7.67 c.c. *N*/10-AgNO<sub>3</sub>. Cl=13.24.

$C_{10}H_{14}ONCl$  requires Cl=13.06 per cent.

##### *$\beta$ -Chloroalloeicinnamic Acid.*

*Ethyl Ester*.—Five grams of the acid were dissolved in 25 grams of absolute alcohol, and dry hydrogen chloride passed in until a 10 per cent. solution was obtained. After boiling on a water-bath for nine hours, the ester was separated in the usual manner. Yield, 4.0 grams. The ester boils at 265° (corr.), with slight decomposition:

0.2022 gave 0.1408 AgCl. Cl=17.22.

$C_{11}H_{11}O_2Cl$  requires Cl=16.85 per cent.

The acid chloride was prepared by adding the theoretical amount of phosphorus pentachloride to a chloroform solution of the acid, warming in a water-bath until the action was completed, and then distilling off the solvent and the oxychloride under diminished pressure. This was not analysed, but was converted into the following derivatives in the usual manner.

*Amide*.—Crystalline needles, melting at  $76^\circ$ :

0.2080 required 11.38 c.c.  $N/10$ -AgNO<sub>3</sub>. Cl=19.38.

0.2690 gave 17.6 c.c. N<sub>2</sub> at  $15^\circ$  and 777 mm. N=7.90.

$C_9H_8ONCl$  requires Cl=19.50; N=7.77 per cent.

*Anilide*.—Colourless, crystalline needles, melting at  $134.5^\circ$ :

0.1324 required 5.16 c.c.  $N/10$ -AgNO<sub>3</sub>. Cl=13.81.

$C_{15}H_{12}ONCl$  requires Cl=13.77 per cent.

*p-Toluidide*.—Crystalline needles, melting at  $142^\circ$ :

0.2014 required 7.63 c.c.  $N/10$ -AgNO<sub>3</sub>. Cl=13.43.

$C_{16}H_{14}ONCl$  requires Cl=13.06 per cent.

The estimation of chlorine was carried out in each case by Stepanoff's method (*Ber.*, 1906, 39, 4056).

In conclusion, I desire to express my thanks to Professor J. J. Sudborough for his interest in the work, and to Mr. Idwal Morgan, B.Sc., for assistance in the preparation and analysis of certain of the compounds.

THE EDWARD DAVIES CHEMICAL LABORATORIES,  
ABERYSTWYTH.

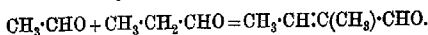
## CLXXXV.—*The Condensation of Crotonaldehyde.*

By IDA SMEDLEY (Beit Memorial Research Fellow).

THE readiness with which aldehydes undergo the aldol condensation in dilute alkaline solutions led Nencki and, later, Magnus Levy to suggest that in the synthesis of fatty acids from carbohydrates which is believed to occur in the animal body, the aldol reaction may take part. Since acetaldehyde may be obtained as a decomposition product of carbohydrates, the production of butyric acid may be assumed to occur by the oxidation and reduction of the aldol formed on condensing two molecules of acetaldehyde. When, however, this hypothesis is applied to explain the formation of the



higher fatty acids, it is no longer in harmony with our knowledge of the aldol reaction; Lieben and his students investigated a large number of aldehyde condensations, and showed that when the higher fatty aldehydes condense, the resulting aldehydes contain branched carbon chains; the hydrogen atom of a CH group was found to react more readily than that of a CH<sub>2</sub> group, the methylene hydrogen more readily than that of a methyl group (*Monatsh.*, 1883, **4**, 10; 1901, **22**, 289). Thus, the interaction of propaldehyde and acetaldehyde leads to the production of tiglic aldehyde,\* and not of the normal chain aldehyde required for the application of this reaction to the synthesis of the fatty acids:



The formation of the unsaturated aldehyde or of the intermediate hydroxy-compound was found to depend on the strength of the alkaline condensing agent used. Previously, Schmidt had described the reaction between furfuraldehyde and propaldehyde as taking place between the furfuraldehyde group and the  $\beta$ -carbon atom of the propaldehyde; no evidence for this was, however, given, and from Lieben's work it appears improbable that the reaction can take place in this direction (Schmidt, *Ber.*, 1881, **18**, 574).

The condensation of aldol was studied by Raper (*Trans.*, 1907, **91**, 1831), who obtained the remarkable result that *n*-octoic acid was produced by reducing with hydriodic acid and phosphorus the acid formed by oxidation of the condensation product of aldol. This involved the condensation of the aldehyde group, with the hydrogen attached to a  $\gamma$ -carbon atom. During the condensation a molecule of water was lost, but evidence was lacking as to how this had been eliminated.

The important modification brought about in the aldol reaction by the introduction of a  $\beta$ -hydroxyl group made it desirable that the influence of other groups should be determined, and the effect of the ethenoid linking on the aldol condensation has, therefore, been examined, crotonaldehyde being chosen for investigation.

The condensation of crotonaldehyde under the influence of acid condensing agents has been investigated by Delépine (*Compt. rend.*, 1910, **150**, 394), who obtained a bimolecular product, C<sub>8</sub>H<sub>12</sub>O<sub>2</sub>, boiling at 86–87°/18 mm., to which he attributed a cyclic formula.

The author has now investigated the action of solutions of potassium acetate, potassium carbonate, potassium hydroxide, sodium hydroxide, and guanidine carbonate in varying concentrations on crotonaldehyde; the most favourable conditions appeared

\* Tiglic acid, although not known as a constituent of fats, occurs plentifully in nature as a constituent of croton oil.

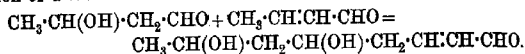
to be obtained by dissolving crotonaldehyde in ten times its volume of *N*/10-potassium carbonate, and leaving the solution for three days at the ordinary temperature. With solutions weaker than *N*/20 and stronger than *N*/5, the reaction proceeded more slowly; at 0° solutions of crotonaldehyde in *N*/10-potassium carbonate underwent very little change in three days. In each case the amount of potassium carbonate was found to be practically unchanged at the end of the experiment. If, however, dilute solutions of the alkali hydroxides were used, a considerable proportion was neutralised during the course of the experiment, the condensation product apparently undergoing the Cannizzaro reaction (compare Lieben, *loc. cit.*). The soluble condensation product decomposed when it was distilled under a pressure of 10–15 mm.; no characteristic crystalline derivatives were obtained from it. By the action of silver oxide an unsaturated hydroxy-acid was obtained, having the formula  $C_8H_{12}O_3$ , which absorbed hydrogen in the presence of finely divided platinum; on treating with hydriodic acid and phosphorus it was converted into octoic acid. The difficulties attending the purification and identification of the condensation product are such that it is not possible to say with any degree of certainty whether it is a single substance or a mixture of isomerides. The proportion of the normal eight-carbon chain present in the condensation product is, therefore, uncertain; the detection of *n*-octoic acid in the reduction product establishes, however, that a compound containing a straight chain of eight-carbon atoms is formed in the reaction.

Raper's work on the condensation of aldol was repeated, and his final reduction product prepared for comparison with the specimen of octoic acid obtained from the crotonaldehyde condensation product. The yields were in both cases very small, that from the aldol product being rather the better; in each case from 40 grams of the barium salt of the unreduced acid about 0.1 gram of the pure amide was obtained, melting at 103–104°; the melting point was unchanged on mixing together, and each was separately mixed with octoamide prepared from Kahlbaum's pure octoic acid, the melting point of each mixture being unaltered (103–104°). When mixed with the amide of ethylhexoic acid (Raper, *loc. cit.*), which melts at 101–102°, the melting point was lowered to 95°. There are considerable differences in the melting points assigned by different observers to octoamide; they range from 99° to 110°; Raper gives 105–106°. After two recrystallisations from water and one from petroleum, the three specimens examined by the author melted at 103–104°. The amide of 1-methylcyclohexane-2-carboxylic acid (m. p. 181°), which might conceivably be formed

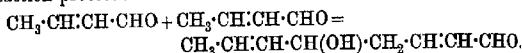
by the conversion of the straight-chain compound into a cyclic compound, as in the case of the olefinic terpenes, was not detected.

The dimethylcyclopentanecarboxylic acid which might be formed from the branched-chain product is not known, but the identification of the octoic acid seemed convincing. Analysis of the amide obtained partly by the reduction of the crotonaldehyde condensation product and partly from the aldol product gave results agreeing with those required for octoamide.

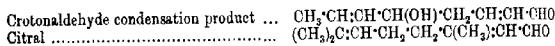
Since in the condensation of aldol a molecule of water is eliminated, it is possible that this reaction really consists of the condensation of a molecule of aldol with one of crotonaldehyde:



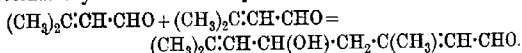
In the case of crotonaldehyde, no water appears to be lost during the condensation, and it may be supposed, therefore, that the reaction proceeds as follows:



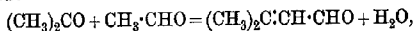
It is interesting to compare this structure with that of the widely-distributed group of olefinic terpene compounds, for example, with citral:



The relative position of the double bonds is the same as in the crotonaldehyde condensation product, and a consideration of the position of the methyl groups suggests that the terpene chain may be produced by an aldol condensation of a methyl derivative of crotonaldehyde similar to that just described:



Such a product differs from citral only in the substitution of a hydroxyl group for a hydrogen atom. The methyl derivative of crotonaldehyde,  $(\text{CH}_3)_2\text{C}:\text{CH}\cdot\text{CHO}$ , required for this condensation has not yet been prepared; it is possible that in the organism acetone and aldehyde may be condensed so as to produce this compound:

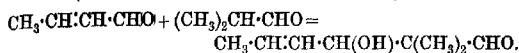


although in the laboratory such a synthesis has not yet been effected.

Raper's synthesis of a normal eight-carbon-chain compound and the synthesis, now described, of the same chain from crotonaldehyde suggest that it may be possible by the introduction of ethenoid linkings or hydroxyl groups so to modify the reactivity of the

compound that the carbonyl group of the higher aldehyde will react with the methyl group of acetaldehyde, and give the normal carbon chains required for the formation of fatty acids.

In the only other case of aldol condensation described in which crotonaldehyde takes part it is perhaps significant that it is the crotonaldehyde carbonyl group that reacts, for the condensation of crotonaldehyde and isobutyraldehyde is described as taking place as follows (Plattensteiner, *Monatsh.*, 1901, 22, 14):



The author is at present engaged in investigating further the condensation of unsaturated aldehydes.

#### EXPERIMENTAL.

Twenty grams of crotonaldehyde prepared by Delépine's method (*Compt. rend.*, 1908, 147, 1316) were dissolved in 200 c.c. of *N*/10-potassium carbonate, and the solution left at the ordinary temperature for three days. After about one hour the solution had become yellow. A small amount of a yellow, insoluble oil separated, and at the end of the third day the odour of crotonaldehyde was much fainter. The solution was diluted with 500 c.c. of water, filtered, and neutralised with hydrochloric acid. Excess of barium carbonate was added, and the liquid distilled in a current of steam for from two to three hours. The filtered solution was then concentrated under diminished pressure, and the residue extracted with ether. The ethereal solution, after being dried and evaporated, left a viscous oil, which was placed in a vacuum desiccator over concentrated sulphuric acid for some days:

0.1882 gave 0.4568  $\text{CO}_2$  and 0.1484  $\text{H}_2\text{O}$ .  $\text{C}=66.21$ ;  $\text{H}=8.77$ .

$\text{C}_8\text{H}_{12}\text{O}_2$  requires  $\text{C}=68.57$ ;  $\text{H}=8.57$  per cent.

The liquid decomposed when distilled under a pressure of 15 mm., and no satisfactory method of further purifying it was found. It reduced Fehling's solution, and deposited a silver mirror on warming with ammoniacal silver nitrate.

In preparing the condensation product for oxidation and subsequent reduction with hydriodic acid, the steam distillation was omitted, and the solution evaporated at about  $50^\circ$ . The amount of the product thus obtained was considerably increased, and the odour of crotonaldehyde could not be detected in it; yet considerable quantities of butyric acid were obtained in the reduction.

*Oxidation with Silver Oxide*.—A solution of 10 grams of the condensation product was added to 40 grams of silver oxide (freshly precipitated and washed by decantation), and 200 c.c. of

*N*/2-barium hydroxide gradually added, the solution being kept cool. After remaining overnight, carbon dioxide was passed into the filtered solution to remove the excess of barium hydroxide. The filtered solution was evaporated to dryness under diminished pressure, extracted with alcohol, the barium salt precipitated by dry ether, and dried at 100°:

0.1858 gave 0.0970  $\text{BaSO}_4$ .  $\text{Ba}=30.68$ .

$(\text{C}_8\text{H}_{11}\text{O}_3)_2\text{Ba}$  requires  $\text{Ba}=30.65$  per cent.

*Reduction with Sodium Amalgam*:—Reduction with sodium amalgam produced a viscous liquid, which was not satisfactorily characterised. It was dried for eight days in a vacuum desiccator:

0.1065 gave 0.2590  $\text{CO}_2$  and 0.0940  $\text{H}_2\text{O}$ .  $\text{C}=66.32$ ;  $\text{H}=9.81$ .

$\text{C}_8\text{H}_{14}\text{O}_2$  requires  $\text{C}=67.60$ ;  $\text{H}=9.86$  per cent.

The product no longer reduced Fehling's solution, nor did it give Schiff's reaction; it still decolorised bromine water, and probably, therefore, contained an unsaturated alcohol.

*Reduction of the Acid  $\text{C}_8\text{H}_{13}\text{O}_3$  by Hydrogen in Presence of Finely-divided Platinum*:—1.8 Grams of the acid (dried in a desiccator) were dissolved in about 10 c.c. of water, and reduced by shaking with finely-divided platinum in contact with hydrogen at 37° under a pressure of between  $1\frac{1}{2}$  and 2 atmospheres. When no more hydrogen was absorbed, the filtered solution of the barium salt was evaporated; a deliquescent salt remained, which was dried at 100°:

0.1454 gave 0.0745  $\text{BaSO}_4$ .  $\text{Ba}=30.12$ .

$(\text{C}_8\text{H}_{13}\text{O}_3)_2\text{Ba}$  requires  $\text{Ba}=30.38$  per cent.

$(\text{C}_8\text{H}_{15}\text{O}_3)_2\text{Ba}$  „  $\text{Ba}=30.11$  „

The weight of hydrogen absorbed was calculated approximately as 0.0264 gram, whilst 1.8 gram of the barium salt would require 0.0322 gram of hydrogen to saturate it completely.

*Reduction with Hydriodic Acid and Red Phosphorus*:—Forty grams of the barium salt,  $(\text{C}_8\text{H}_{11}\text{O}_3)_2\text{Ba}$ , were heated for five hours with 320 grams of hydriodic acid solution (D 1.7) and 12 grams of red phosphorus. The mixture was diluted, and extracted with ether. After evaporating off the ether, the residual oil was left for twenty-four hours with zinc dust and dilute sulphuric acid, and then distilled in a current of steam. The distillate was neutralised with sodium hydroxide,\* extracted with ether, and the ethereal solution evaporated to dryness; about 5–6 grams of a sodium salt were obtained, from which 4–5 grams of acid were isolated. On distillation, about 3–4 grams passed over below 200°.

\* The ethereal extract contained a small quantity of a neutral oil with an aromatic odour; this was not further investigated.

and about 1 gram above 200°. The residue in the flask was converted into the barium salt:

0.1302 gave 0.0726 BaSO<sub>4</sub>. Ba = 32.78.

(C<sub>8</sub>H<sub>16</sub>O<sub>2</sub>)<sub>2</sub>Ba requires Ba = 32.39 per cent.

The fraction boiling below 200° consisted mainly of butyric acid. (Found, C = 53.57; H = 9.34. Calc., C = 54.54; H = 9.09 per cent.)

The fraction boiling above 200° was analysed:

0.1190 gave 0.2732 CO<sub>2</sub> and 0.1203 H<sub>2</sub>O. C = 62.69; H = 10.11.

0.1450 " 0.3340 CO<sub>2</sub> " 0.1295 H<sub>2</sub>O. C = 62.84; H = 9.93.

C<sub>4</sub>H<sub>8</sub>O<sub>2</sub> requires C = 54.54; H = 9.09 per cent.

C<sub>8</sub>H<sub>16</sub>O<sub>2</sub> " C = 66.66; H = 11.11 "

This fraction was probably, therefore, a mixture of butyric and octoic acids, and was converted into the amides by Aschan's method (Ber., 1898, 31, 2348). The small amount of amide formed was recrystallised from petroleum and twice from water; about 0.1 gram (m. p. 103—104°) was thus obtained.

Raper's work on the condensation of aldol was repeated, and the same amide obtained in slightly larger amount; a mixture of the two amides melted at 103—104°. Each was separately mixed with a specimen of octoamide, prepared from Kahlbaum's pure octoic acid, and in neither case was there any lowering of the melting point; each amide was then added to ethylhexoamide (m. p. 101—102°), when the melting point fell to 96°.

The specimens of octoamide obtained from aldol and crotonaldehyde were now added together and analysed:

0.0754 gave 0.1845 CO<sub>2</sub> and 0.0810 H<sub>2</sub>O. C = 66.74; H = 11.94.

C<sub>8</sub>H<sub>17</sub>ON requires C = 67.13; H = 11.88 per cent.

LISTER INSTITUTE OF PREVENTIVE MEDICINE,  
CHELSEA GARDENS, S.W.

## CLXXXVI.—*Latent Heats of Vaporisation of Mixed Liquids. Part I.*

By DAN TYRER.

THE physical properties of mixed liquids have, for the most part, been fairly completely studied, and the general result that has been discovered is that for normal mixtures of unassociated liquids, the physical properties, as a general rule, are approximately linear functions of the composition, and in the cases of mixtures of associated liquids deviations from this additive law appear. One

physical property, however, seems to have been completely neglected, namely, the latent heat of vaporisation. It is not known whether or not the latent heat of a normal mixture is an additive quantity. When a mixture of two liquids is boiled, both its temperature and composition vary as the vaporisation proceeds, and hence its latent heat must also vary. It is clearly necessary to define the meaning of the latent heat of a mixture. Now a mixture of two liquids has, in two perfectly legitimate senses, two latent heats of vaporisation defined as follows:

(1) The latent heat of vaporisation of a mixture of two liquids is the heat required to evaporate one gram from an infinitely large quantity of the mixture of definite composition.

(2) The latent heat of a mixture of two liquids is the heat required to vaporise completely one gram of the mixture at constant temperature.

In the first definition no regard is paid to the composition of the vapour. Since an infinitely large quantity of the liquid is taken, both the temperature and composition of the parent liquid remain constant.

In the second definition the composition of the vapour is the same as the liquid, since all the liquid started with is assumed to have been vaporised. In order that the vaporisation may take place at constant temperature, the external pressure must be continually diminished as the vaporisation proceeds.

Since in the first case the external pressure is constant, we may term it the latent heat of vaporisation at constant pressure, and denote it by the symbol  $L_p$ .

In the second case the composition of vapour and liquid are the same, so we may term it the latent heat of vaporisation with constant composition, and denote it by  $L_c$ .

That the two quantities are quite separate and different in magnitude may be shown as follows:

Consider an infinitely large quantity of a mixture of two liquids  $A$  and  $B$  at its boiling point  $T$ . Let the composition in terms of the constituent  $A$  be  $C$ . Let one gram be evaporated, say, to avoid complications, under a negligibly small external pressure. The heat absorbed is  $L_p$ .

Now take one gram of the same mixture, and allow it to evaporate slowly in a vacuum at the same temperature  $T$ . Imagine the vaporisation to proceed in infinitely small successive quantities each of mass  $dm$ . The heat required to evaporate the first elementary portion will obviously be  $L_p dm$ . Let us suppose, in the first place, that the constituent  $A$  is the one of higher boiling point, and also possesses the higher latent heat. Then as the evaporation of the

gram of liquid proceeds, the composition in terms of  $A$  will increase, and hence the heat required to vaporise successive elementary portions will continually increase until the heat required to evaporate the last portion will be  $L_A dm$ , where  $L_A$  is the latent heat of vaporisation in a vacuum of pure  $A$  at the temperature  $T$ .

Obviously, the total heat required to vaporise the gram of liquid of composition  $C$  is equal to

$$L_c = - \sum_{L=L_A}^{L=L_p} L dm,$$

and must be much greater than  $L_p$ .

Expressing  $L$  as a function of the mass  $m$  of the unevaporated liquid, we can write:

$$L_c = \int_0^1 f(m) dm.$$

If, on the other hand, the constituent of higher boiling point,  $A$ , has the lower latent heat at the temperature  $T$ , the heat required to vaporise successive fractions will continually diminish, and  $L_p$  will be greater than  $L_c$ .

In this work latent heats at constant pressure ( $L_p$ ) only have been measured.

#### *Method of Determination and Apparatus.*

The latent heat of a pure liquid is a quantity which is by no means easy of measurement with accuracy, as a comparison of results obtained by different observers for the same liquid will show. With mixed liquids the difficulties are increased, for account has to be taken of changing composition and changing temperature as the vaporisation proceeds. There are two general methods of determining latent heats which have been fully worked out, namely, (1) condensation of vapour in a calorimeter, and observation of the heat evolved; (2) measurement of heat required to vaporise, by an electrically-heated wire, a weighed quantity of a liquid. An adaptation of the second method to mixed liquids is described in this paper.

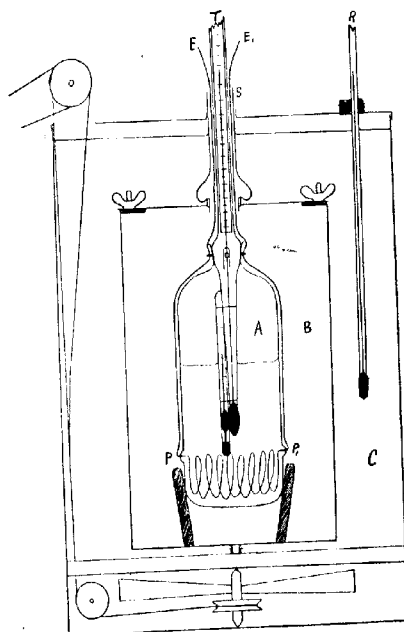
The general principle of the method adopted is as follows: A known quantity of electricity is passed through a coil of platinum wire of known resistance, which is immersed in the liquid the latent heat of which is to be measured, first heated to its boiling point by an external bath. The amount of liquid evaporated is found by weighing before and after. This gives all the data necessary.

When, however, a mixed liquid is partly evaporated, the boiling point rises, and a certain amount of heat is used up in raising the



temperature of the liquid. To determine this correction a separate experiment is made to find the heat capacity of the liquid and the containing vessel, and the total rise in temperature is found by having a thermometer dipping into the liquid. In order that this rise in temperature may be small, a comparatively large quantity of the liquid is taken, and only a small quantity evaporated.

FIG. 1.



The general form of the apparatus is shown in the accompanying diagram.

The liquid the latent heat of which is to be measured is placed in the evaporating bottle *A*, which is about 250 c.c. capacity. This bottle is provided with a coil of platinum wire (about 1 metre of 0.02 cm. diameter), the ends of which are fused to two stout pieces of platinum, which are fused through the sides of the bottle at the points *P*, *P*<sub>1</sub>. Stout pieces of copper wire are soldered to the platinum terminals, and pass outside to the ends *E*, *E*<sub>1</sub>, which can

be attached to circuit leads. A thermometer  $T$  is ground into the neck of the bottle, and has a groove impressed in it, which can be turned opposite to a small hole pierced in the neck of the bottle, thus allowing it to be opened or closed to the external pressure. The bottle is made to stand on rubber-covered rods, as shown, in a copper insulating vessel  $B$ . This vessel is provided with a lid and two windows front and back (not shown in sketch). The lid and the panes of glass of the windows are screwed down on rubber to render the vessel perfectly water-tight. The vessel  $B$  is pivoted inside a large bath  $C$ , made of sheet copper, and provided with two windows (not shown). It contains water (or for temperatures higher than  $100^{\circ}$ , a high boiling liquid), and is heated by burners from below. It is provided at the bottom with a rotatory stirrer connected by a cord passing over pulleys to a small motor outside. The temperature of this bath is registered by a thermometer  $R$ . The vessel  $B$  can be rotated rapidly backwards and forwards by turning the glass tube  $S$ , and this serves to give the liquid in the evaporating bottle a rotatory motion, and continually sweeps fresh liquid over the platinum coils as the evaporation proceeds. Inside the bottle, attached to the thermometer, is a very small manometer, which serves to indicate when the pressure in the bottle has reached the atmospheric pressure.

The thermometers  $T$  and  $R$  are graduated in  $1/5$ ths, and are readable to  $0.02^{\circ}$  with accuracy.

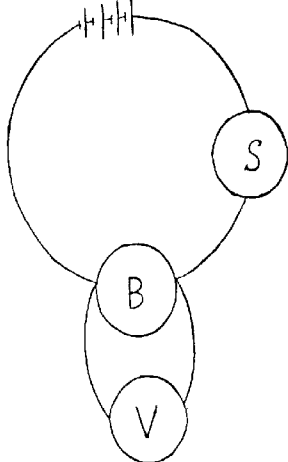
The current used is obtained from secondary cells (about eight cells are necessary), and is quite steady. The current passed through the circuit is accurately measured by means of a silver voltameter. The general arrangement of the apparatus is indicated in the accompanying diagram.

$S$  is the silver voltameter,  $B$  is the evaporating bottle, and  $V$  is a Weston voltameter to measure the potential difference between the terminals of the platinum coil. This latter instrument covers a range of 8–13 volts, is graduated in 0.05 volt divisions, and is readable with accuracy to less than 0.01 volt. All the electrical contacts, where possible, were soldered to ensure perfect contact, and the switches were made tight, and were of a heavy type. The contacts were quite without resistance.

The composition of the mixed liquid is found before and after an experiment by determining the specific volumes of the liquid at a constant temperature, a table having been prepared beforehand, representing the relation between the composition and the specific volume. The specific volumes were determined with a quartz pycnometer immersed in a thermostat at about  $20^{\circ}$ , and the measurements were made to the fifth decimal place. The calculated

compositions contain an error not greater than 0.01 unit for mixtures the constituents of which differ moderately in their densities, whilst for mixtures like chloroform and benzene, which show a large variation of specific volume, an even greater degree of accuracy is obtained. About 5 to 12 grams of liquid are evaporated in each experiment. With mixtures like carbon tetrachloride and ether this causes a variation in composition of about 2 units, but with chloroform and benzene the variation is only about 0.2 unit. It is then assumed that over this small range the latent heat is a linear function of the composition, and the mean com-

FIG. 2.



position is taken as the point for which the latent heat is as determined in the experiment. The error of this assumption is negligibly small.

In carrying out an experiment, the boiling point of the mixed liquid is first determined approximately, and then its composition is found by determining with accuracy its specific volume. The evaporating bottle is about two-thirds filled, and weighed. The air is then pumped out of the bottle by pressing the end of the rubber tube which is attached to a strong water pump against the open orifice in the neck of the bottle, and when the liquid has boiled for a few seconds closing the bottle by turning the thermometer stem. The ground joint at the neck is lubricated with a

mixture of fused dextrose and glycerol. This lubricant is quite insoluble in organic solvents, and when made up to a proper consistency it answers the purpose admirably. It has the advantage over phosphoric acid as a lubricant, that it is more adhesive, and is not so easily squeezed out by pressure. It is also hygroscopic, but not to so great a degree as phosphoric acid.

After the air has been pumped out of the bottle it is again weighed to determine loss of liquid during the evacuation. A small correction is made to account for the very small change in the composition caused by this loss. The bottle is then placed in position in the inner copper vessel, and the external bath is heated to the boiling temperature of the mixture. The bottle and contents are slowly warmed by the passage through the platinum coil of a small shunted current. When the pressure inside the bottle has reached the external atmospheric pressure, as is indicated by the small manometer inside the bottle, and it has remained at a constant temperature for some minutes, the bottle is opened by turning the thermometer stem. The current is then switched on, and the boiling should commence immediately. The potential difference between the ends of the platinum coil should be from about 10 to 12.5 volts. As the temperature rises (usually about 1—1.5°) the temperature of the outside bath is raised correspondingly. A difference of a few tenths of a degree between the temperature of the boiling liquid and the outside bath makes no material difference during the time of an experiment, which only lasts about four or five minutes. As the boiling proceeds it is observed that the needle of the voltmeter always falls slightly, but this is only small (about 0.8 per cent.), and by taking readings at regular small intervals and finding the mean, the error in the voltage is reduced to about 0.07 per cent.

The total current passed through the coil is found by weighing the silver deposited on the platinum basin of the voltmeter. About 0.3 to 0.45 gram of silver is usually deposited, and the error in weighing is not greater than 0.1 milligram. The temperature of the bath and bottle is allowed to fall about 3°, and the experiment is repeated with the bottle closed, and with a voltage of about 8.5. The rise in temperature is observed (about 4°), and the range covers that through which the temperature rose in the first experiment. This gives the heat capacity of the bottle and contents. The bottle is then weighed to determine the amount of liquid vaporised in the first experiment.

The latent heat is then calculated from the following equation:

$$L = \frac{J.S.V.}{A.M.}$$

where  $L$  is latent heat,  $J$  is electrical heat equivalent,  $S$  is weight of silver deposited during the experiment,  $V$  is the volts recorded on the voltmeter,  $A$  is the electrochemical equivalent of silver, and  $M$  is the weight of liquid vaporised.  $M$  is equal to the loss in weight of the bottle + the weight of vapour occupying the space vacated by the vaporised liquid at the boiling point. The latter, which is a small correction, can be approximately calculated.

A correction has now to be subtracted for the heat required to raise the temperature of the liquid during the vaporisation. This is:

$$H = \frac{C \times t \times W}{M},$$

where  $C$  is the heat capacity of liquid and bottle,  $t$  is the rise in temperature observed, and  $W$  is the mean weight of bottle and contents.  $C$  is found from the second experiment, and is given by:

$$C = \frac{J \times S_1 \times V_1}{A \times t_1 \times W_1},$$

where  $S_1$  is weight of silver deposited,  $V_1$  the voltage,  $t_1$  the rise in temperature, and  $W_1$  is the final weight of bottle and contents.

The corrected latent heat is then given by the following:

$$L_p = \frac{J}{A.M.} \left( SV - \frac{t}{t_1} \cdot \frac{W}{W_1} \cdot S_1 V_1 \right).$$

The correction need not exceed about 6 units, and is known with accuracy. The constant  $J/A$  has the value 213.60.

Three mixtures have been investigated, namely, ether and carbon tetrachloride; benzene and *n*-hexane; chloroform and benzene.

The results obtained are set forth in the remaining portion of the paper.

An idea of the general accuracy and practicability of the method is obtained by a comparison of results obtained for pure liquids with standard results obtained by other investigators.

The values given in the following tables for the latent heats refer to a mean pressure a few mm. above 760 mm. Without knowing variation of latent heat with variation of atmospheric pressure it is impossible to reduce all the values to one standard pressure. The difference, however, caused by a moderate change in external pressure makes but a very slight difference to the latent heat. The error is in any case well within total error of results.

#### *Mixtures of Benzene and n-Hexane.*

The benzene used in these experiments was prepared from Kablaum's pure material by refractionation over phosphoric oxide. It

was quite free from thiophen, and a litre distilled at constant temperature. Its specific volume at  $20.00^{\circ}$  was 1.13815.

Kahlbaum's pure hexane from petroleum was refractionated. Its specific volume at  $20.00^{\circ}$  was 1.47471.

*Latent Heat of Benzene*:—Three consecutive experiments gave the results:

	94.43 calories
	94.31    "
	94.31    "
Mean.....	94.35    "

These values refer to a mean pressure of 763 mm., and a temperature of  $80.35^{\circ}$ . Griffiths and Marshall (*Phil. Mag.*, 1896, [v], **41**, 1) obtained the value 94.37. This result is probably the most accurate latent heat determination that has been made. J. C. Brown (*Trans.*, 1905, **87**, 265) obtained the result 94.93.

*Latent Heat of Hexane*:—Two consecutive results gave:

	81.59 calories
	82.11    "
Mean.....	81.85    "    Temperature = $66.88^{\circ}$ .

Mabery and Goldstein (*Amer. Chem. J.*, 1902, **28**, 66) obtained the result 79.4, which is rather considerably lower than the above.

*Latent Heats of Mixtures of Benzene and Hexane*:—The experimental results were plotted on cross-section paper against the composition, and the results given in the following table were read off from the smoothed curve. In the table also is given the boiling points of the mixtures for a mean pressure of about 766 mm.

Percentage of $C_6H_6$ in the mixture.	Latent heat in calories.	Boiling point.	Percentage of $C_6H_6$ in the mixture.	Latent heat in calories.	Boiling point.
0	81.85	$66.88^{\circ}$	60	85.60	$71.3^{\circ}$
10	81.93	67.55	70	87.20	73.2
20	82.15	68.6	80	89.03	75.1
30	82.55	69.1	90	91.27	77.4
40	83.24	69.9	100	94.35	$80.45^{\circ}$
50	84.26	70.8			

The above results for the latent heats of the mixtures contain estimated accidental errors of about 0.05 unit, but the series may contain a constant error of about 0.2 unit. The results are discussed at the end of the paper.

#### *Mixtures of Carbon Tetrachloride and Ether.*

Kahlbaum's carbon tetrachloride was refractionated; its specific volume at  $20^{\circ}$  was 0.62724. The ether used was prepared from absolute alcohol in the ordinary way. It was purified by washing

with acid, alkali, and water, and drying over calcium chloride and sodium. It was then fractionated, dried further over phosphoric oxide, and again fractionated; 500 c.c. distilled over constantly within  $0.01^{\circ}$ . Its specific volume at  $20^{\circ}$  was 1.40154 (Ramsay and Young's value=1.4015).

*Latent Heat of Carbon Tetrachloride*:—Three consecutive results gave:

	47.04 calories
	46.86   "
	46.84   "
Mean.....	46.85   "   Temperature= $77.75^{\circ}$ .

The first result was considered rather less accurate than the other two, and is excluded from the mean value.

Wirtz (*Wied. Ann.*, 1890, **40**, 446) obtained the result 46.35.

*Latent Heat of Ether*:—Three experiments gave the values:

	86.74 calories
	86.06   "
	86.52   "
Mean.....	86.44   "   Temperature= $34.74^{\circ}$ .

The following are results by other observers:

Wirtz ( <i>Wied. Ann.</i> , 1890, <b>40</b> , 438) ...	88.39 calories.
Brown ( <i>Trans.</i> , 1903, <b>83</b> , 987) ...	84.78   "
Ramsay and Young ( <i>Phil. Trans.</i> , 1887, <b>178</b> , A, 90) ...	84.5   "
Brix ( <i>Pogg. Ann.</i> , 1842, <b>55</b> , 341) ...	90.0   "
Andrews ( <i>Quart. Journ. Chem. Soc.</i> , 1849, <b>1</b> , 27) ...	90.45   "
Favre and Silbermann ( <i>Compt. rend.</i> , 1846, <b>23</b> , 413) ...	91.11   "

The results for ether appear to be very discordant. The latent heat of ether seems to be greatly affected by small amounts of impurities.

*Latent Heats of Mixtures of Carbon Tetrachloride and Ether*:—

The following results were read from a smoothed curve of experimental values:

Percentage of carbon tetrachloride in mixture.	Latent heat in calories.	Boiling point.	Percentage of carbon tetrachloride in mixture.	Latent heat in calories.	Boiling point.
0	86.44	$34.75^{\circ}$	60	76.75	$47.25^{\circ}$
10	86.30	$36.15$	70	73.00	$50.80$
20	85.50	$37.60$	80	68.47	$55.77$
30	84.05	$39.40$	90	61.60	$64.65$
40	82.15	$41.65$	100	46.85	$77.75$
50	79.35	$44.25$			

The above results are similar in point of accuracy to those in the previous case.

*Mixtures of Chloroform and Benzene.*

The chloroform was prepared from commercially "pure" material as follows. It was washed with acid, alkali, and water, and then distilled under a layer of dilute alkaline solution of potassium permanganate. The product was dried over calcium chloride, fractionated, dried further over phosphoric oxide, and again fractionated. About 2 litres distilled over within 0.03°. Its specific volume at 20° was 0.67219, and it boiled at 61.40°/758 mm.

*Latent Heat of Chloroform:*—Three experiments gave the results:

	59.38 calories
	59.27    ,,
	59.24    ,,
Mean.....	59.29    ,,    Temperature = 61.52°.

Wirtz (*Wied. Ann.*, 1890, **40**, 446) obtained the value 58.49.

Data concerning the benzene have already been given.

*Latent Heat of Mixtures of Chloroform and Benzene:*—The results given in the following table were obtained from a smoothed curve of experimental results.

Percentage of chloro- form in the mixture.	Latent heat in calories.	Boiling point.	Percentage of chloro- form in the mixture.	Latent heat in calories.	Boiling point.
0	94.35	80.65°	60	70.13	71.75°
10	90.00	79.58	70	67.15	69.50
20	85.55	78.40	80	64.50	67.00
30	81.25	77.12	90	61.83	64.30
40	77.15	75.58	100	59.29	61.52
50	73.40	73.80			

*Discussion of Results.*

The relation between the latent heat at constant pressure and the composition is best shown graphically.

It will be seen from the figure that the latent heat is by no means a linear function of the composition, as might have been expected. There is a relation which holds fairly closely in two cases between the latent heat and the boiling point. This can be shown by testing the well known relation of Trouton:

$$\frac{LM}{T''} = K,$$



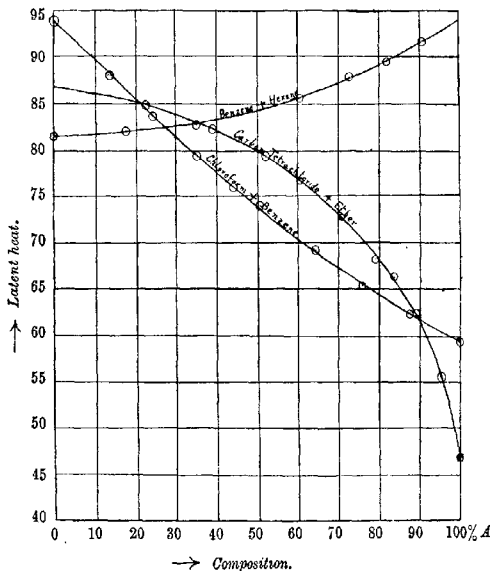
where  $L$  is the latent heat,  $M$  the molecular weight, and  $T$  is the temperature of boiling on the absolute scale.

In the case of mixtures,  $M$  must be taken as the mean molecular weight given by the formula:

$$M = \frac{100}{\frac{C}{M_A} + \frac{100-C}{M_B}}$$

where  $C$  is the composition in terms of the constituent  $A$ , and  $M_A$  and  $M_B$  are the molecular weights of the pure constituents. In

FIG. 3.



the following table are given the values of the constant  $K = LM/T$  for the three cases.

While the value for  $K$  in the first and third cases is fairly constant, there is an entire lack of constancy for the case of carbon tetrachloride and ether.

Now Trouton's equation is directly deducible from the relation:

$$LM = K_1 T \log \frac{V_2}{V_1},$$

Composition C.	Values of $K$ for mixtures of benzene and hexane.	Values of $K$ for mixtures of carbon tetrachloride and ether.	Values of $K$ for mixtures of chloroform and benzene.
0	20.74	20.85	20.83
10	20.51	21.86	20.66
20	20.31	22.75	20.42
30	20.15	23.60	20.24
40	20.07	24.40	20.05
50	20.07	25.08	20.01
60	20.13	25.77	20.04
70	20.23	26.23	20.24
80	20.35	26.36	20.48
90	20.52	25.34	20.84
100	20.83	20.55	21.06

where  $T$  is the temperature,  $V_v$  and  $V_L$  are the specific volumes of vapour and liquid respectively at  $T$ , and  $K_1$  is a constant. This relation, moreover (see Crompton, *Proc.*, 1901, 17, 61; and Klee-man, *Phil. Mag.*, 1910, [vi], 20, 665), depends on the assumption that the composition of the vapour is the same as that of the liquid. We should expect, therefore, that Trouton's equation will only hold for mixtures when the difference between the composition of the liquid and the saturated vapour is comparatively small. Of the above cases this difference is greatest in the case of carbon tetrachloride and ether, and this case, as has been seen, shows the greatest divergence.

It is fairly clear that the latent heat of a liquid at constant pressure, although it is a function of the composition of the mixed liquid, is, at the same time, largely a property of the vapour, and dependent on the composition of the vapour.

It is hoped in subsequent papers to extend the present investigations to other classes of mixtures, and to study the relation between the latent heat and the composition of the vapour which is in equilibrium with the liquid of known composition.

The author is indebted to Mr. J. I. Crabtree, B.Sc., for much valuable assistance in the early stages of the work.

THE CHEMICAL LABORATORIES,  
THE UNIVERSITY, MANCHESTER.

## OBITUARY NOTICES.

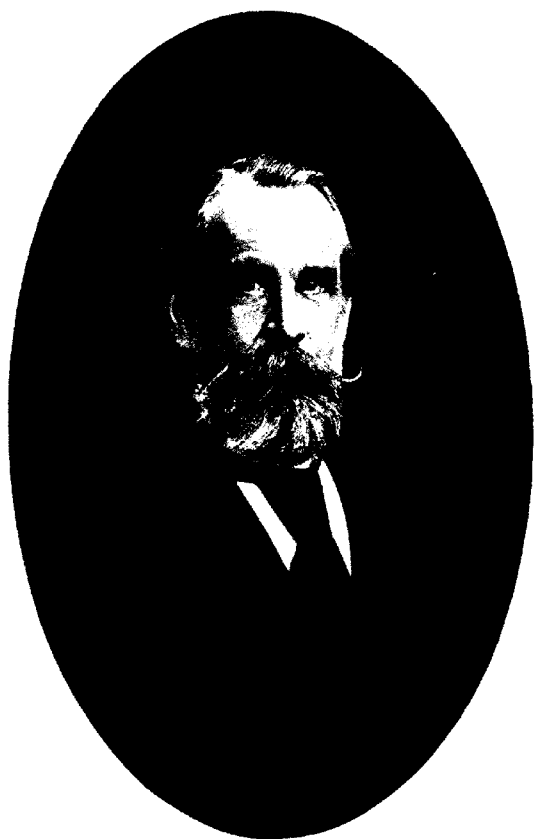
## FRIEDRICH KONRAD BEILSTEIN.

BORN FEBRUARY 17TH, 1838; DIED OCTOBER 18TH, 1906.

THE honorary membership of the great learned societies is a testimony of admiration for the brilliant work done by the recipients. In the case of Beilstein it was more; it was, above all, an expression of deep personal gratitude of innumerable chemists, whose own scientific work had been in no small way advanced and helped by that most marvellous product of an unusually clear and systematic mind, Beilstein's "Handbuch der Organischen Chemie." To the production of this book Beilstein not only devoted his whole life, but he also sacrificed, especially in later years, many opportunities for original experimental work, which, if he had been able to utilise them, would have materially added to his claims for our admiration as a master of experimental research.

Born on February 5/17th, 1838, in St. Petersburg, Beilstein was, like so many of the inhabitants of the great northern capital, German by descent, but a Russian in his nationality and his complete mastery of the difficult language of his adopted country. After receiving his first education in one of the excellent German schools of his native city, he left, a very precocious youth of only fifteen years of age, for Heidelberg, where he studied chemistry under the excellent tuition of Bunsen. After two years he moved to Munich, and became a pupil of Liebig. Very soon, however, he returned to Heidelberg, where he had occasion to join that remarkable group of distinguished young scientists then living in that beautiful city—Roscoe, Lothar Meyer, Landolt, Pebal, Lieben, Quincke, Baeyer, and others. In animated discussions with these and other friends Beilstein gradually acquired the interest and preference for organic chemistry, which henceforward became the special domain of his own scientific research.

It was this increasing love for the problems of organic chemistry which led him once more to change his place of residence and to move to Göttingen, where Wöhler, then still in the prime of his life and scientific activity, attracted a large circle of enthusiastic admirers and collaborators. Following in the great master's footsteps, Beilstein began his own research work with investigations in the cyanogen group, one of which, an elegant study of murexide,



*F. Beilstein*



he used as a dissertation for taking his degree as a Ph.D. in February, 1858, two days before completing his twentieth year.

Beilstein was ever anxious to increase his skill and experience. With the intention of so doing, he went to Paris, and there became an assiduous pupil of Adolphe Wurtz in his laboratory in the École de Médecine. Here he associated with Friedel, and his work during this period, referring to the action of sodium ethoxide on ethyl and other acetates, bears testimony of this friendship. At the same time he went deeper and deeper into the study of chemical theories, until he decided to devote his whole life to pure science and to an academical career.

With this intention Beilstein accepted a situation as laboratory assistant at Breslau offered to him by Loewig in the autumn of 1859, but he soon exchanged it for a better one at Göttingen. Here he remained for six years, until 1866, when he was called back to St. Petersburg to fill a professorship in his native city.

Beilstein's official position in Göttingen was that of a laboratory assistant, but he soon obtained the "*venia legendi*," and lectured as a "*Privatdocent*" on organic chemistry. In 1865 the faculty conferred on him the dignity of a "*Professor extraordinarius*." Beilstein's life in Göttingen was one of incessant activity as a teacher and an investigator. He was connected by intimate friendship with his colleagues Fittig and Hübner, and jointly with them he accepted the task of editing the *Zeitschrift für Chemie*, founded by Kekulé, and important to this day as a source of information.

Here in Göttingen Beilstein found that field of experimental research which was destined to prove most fruitful in his hands, the study of the isomerism of the derivatives of the benzene series. He began this work with the brilliant discovery of the relations existing between chlorotoluene and benzyl chloride. He then embarked on an elaborate investigation of the isomerism existing between the various chlorinated benzoic acids and other members of the aromatic group. Occasionally he also turned his attention to problems of the aliphatic series.

It was in Göttingen that Beilstein began to collect the systematic notes on organic compounds which finally led to the production of his famous handbook. No doubt they were originally only meant for his own information and reference, but he took an ever-increasing pride and pleasure in keeping them complete in spite of the rapid growth of the chemical literature, and in later years he became aware of their extraordinary value and utility as a work of reference for all chemists engaged in the investigation of organic compounds. He found an able publisher in the firm of Leopold

Voss, in Hamburg. The first edition, which Beilstein compiled practically without help, appeared in 1881 in two volumes, and was rapidly exhausted. The second edition began to appear in 1886, and filled three volumes of larger size than the first; the third edition was commenced in 1893, and its four volumes may almost be called unwieldy. It was finished in 1900, and has been supplemented, as everyone knows, by four large volumes of additions edited by the German Chemical Society, which became the proprietor of the handbook and the heir to Beilstein's immortal creation. The fourth edition, now in progress, is expected to assume the size of a small library.

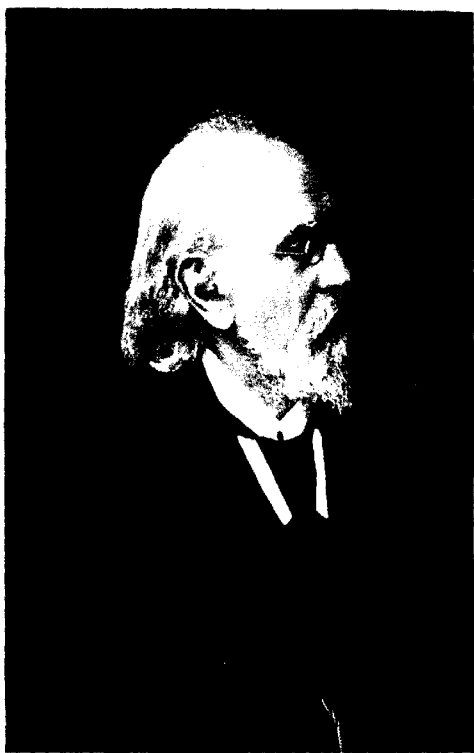
Beilstein's handbook is, in its completeness, its short and concise, yet exhaustive, wording, the most perfect work of reference ever compiled for any domain of human knowledge. At the same time it forms a faithful mirror representing the extraordinary growth of research in the field of organic chemistry. Already the handbook itself has grown, in spite of the marvellous clearness of its system, too large to be used in the ordinary way of referring to such books. But supplemented, as it now is and for ever will be, by Richter's equally marvellous index, it will hold its own in future days as a brilliant proof that even the most complicated subjects may be clearly registered by a systematic genius such as it was the good fortune of chemical science to possess in Beilstein.

In 1866 Beilstein returned to his native country, where he became Professor of Chemistry at the Imperial Technological Institute of St. Petersburg. As an investigator he continued in his new position the work to which he had devoted himself in Göttingen. Jointly with a few collaborators, such as Kuhlberg, Kurbatoff, and others, he published a large number of researches of lasting value, referring almost exclusively to the phenomena of isomerism of the aromatic series.

In 1881 Beilstein became a member of the Russian Academy of Sciences, a position with which is associated a good income, a private dwelling, and a laboratory. He was soon able to retire from his professorship, and to live entirely for research, the compilation of his handbook, and his favourite pastime, music. He was also very fond of travelling, and invariably spent several months of the year in Germany and other countries of Europe. After visiting his old friends and making new acquaintances in the chemical world, he generally settled himself in some beautiful spot in the Tyrol or in Switzerland, studying the lovely scenery of the mountains, but never omitting to devote several hours a day to the handbook which had become an integral part of his life. He almost seemed to have lost something, when, in 1900, this work came, for him, to an end,







*D. C. Lammeyer*

and passed entirely into the hands of the German Chemical Society.

Beilstein remained a bachelor all his life, but he had an adopted daughter, who was his companion in later years, when, by losing some of his best friends, he began to feel solitary. In 1904 this young lady married an officer of a regiment stationed at Kiew. In 1905 Beilstein took a long journey to France, followed by a stay at Baden-Baden. For 1906 he planned a stay at the Riviera, but Fate would have it otherwise. On October 5/18th, 1906, he died quite suddenly in an apoplectic attack.

Beilstein was a genial and most amusing companion, full of humour, and inclined to be caustic and sarcastic, although good-natured, in his quaint and witty remarks on mankind and its doings. He had a brilliant memory, and an inexhaustible fund of information on every possible subject. His life was a beautiful example of devotion to science; it was well spent, and well filled by the fixity of its purpose.

OTTO N. WITT.

#### EMIL ERLÉNMEYER.

BORN JUNE 28TH, 1825; DIED JANUARY 22ND, 1909.

RICHARD AUGUST CARL EMIL ERLÉNMEYER, whose death occurred on January 22nd, 1909, was the son of Dr. Friedrich Erlénmeyer, a Protestant divine, and was born in Wehen, near Wiesbaden, on June 28th, 1825. After passing his Maturitäts Examination in 1845, his intention was to study medicine, and, with this object in view, he proceeded to the University of Giessen, where he attended Liebig's lectures, which, together with the personality of Liebig, had such an effect on the young student that he soon decided to devote himself entirely to chemistry. In the summer of 1846 he went to Heidelberg for one year, and studied physics, botany, and mineralogy under Jolly, Bischof, and Leonhardt, returning to Giessen in 1847.

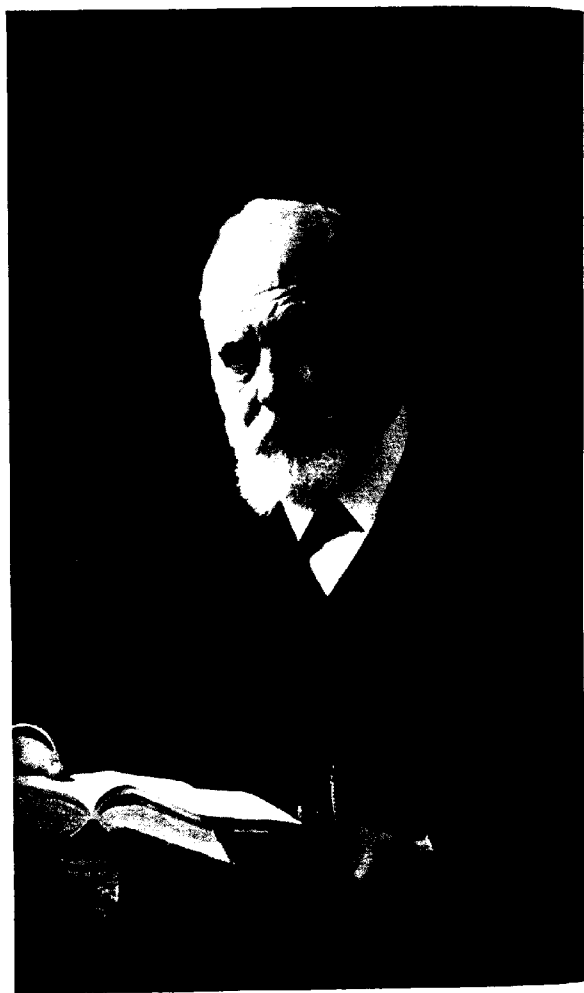
After serving as assistant to H. Will, and subsequently in the same capacity to Fresenius, Erlénmeyer decided to devote himself to pharmaceutical chemistry, and to this end he studied in Nassau, where he passed the State pharmaceutical examination, and shortly afterwards acquired an apothecary's business, first at Katzenellenbogen, and subsequently in Wiesbaden. Pharmacy appears to have had no charm for Erlénmeyer, and, in order to follow the career of a teacher, he graduated in Giessen in 1850, and in 1855 proceeded to Heidelberg in order to devote himself entirely to chemistry. There he converted a shed into a private laboratory,

in which he carried out investigations for weeks, and, in the capacity of expert, he had frequent occasion to visit France and England. In 1857 Erlenmeyer became "Privatdozent," and his thesis, "on the manufacture of the artificial manure known as superphosphate," contained a description of several crystalline substances which greatly interested Bunsen. It was while at Heidelberg that Erlenmeyer was brought under the influence of Kekulé, whose theoretical views he was one of the first to adopt, and subsequently, on the removal of Kekulé to Ghent in 1859, his laboratory became the centre of organic chemistry in Heidelberg. The success of his teaching led the University of Heidelberg to make him extraordinary Professor in 1863, and in 1868 he was called to Munich to take charge of the fine laboratories of the new Polytechnic School, a post which he held until his retirement from teaching in 1883. During these years he worked with ceaseless energy as an investigator, and especially as a teacher, and the success of his teaching was doubtless due in great measure to the amount of time and energy which he devoted to the personal instruction, not only of the advanced students, but also of beginners. Many of Erlenmeyer's most valuable publications deal with problems of theoretical chemistry, and in most of these the influence of Kekulé is very marked; two of his most important achievements are doubtless the suggestion of the formula for naphthalene, which is still in use, and his statement of the well-known law, to which his name became attached. According to this law, unsaturated alcohols,  $>\text{C}:\text{CH}\cdot\text{OH}$  and  $>\text{C}:\text{C}(\text{OH})\cdot\text{C}<$ , are incapable of existence, and are converted, at the instant of formation, into aldehydes and ketones by intramolecular change, a law which does not now hold good in all cases, but which, at that time, was a true statement of the facts as they were then known.

Erlenmeyer's practical investigations were concerned mostly with problems in the aliphatic series. In 1859 he succeeded in synthesising aminohexonic acid, an important investigation, which led him to study the general behaviour of albuminoids on hydrolysis. He worked out methods which enabled him to determine the relative amounts of leucine and tyrosine which are produced during the degradation of several substances of this class, and these researches, carried out with great care and skill, may be said to have served as models for other investigators in the same field.

He was the first (1860) to understand clearly the nature of glycide, and to suggest that this substance is related to glycerol in the same way as is metaphosphoric acid to orthophosphoric acid; in the following year he studied the action of hydriodic acid on glycerol, and showed that the product is isopropyl-, and not propyl-,





*Fisig.*

iodide, as ~~was first~~ <sup>was first</sup> ~~ascertained~~. In ~~reaction~~ <sup>reaction</sup> with Wanklyn, he subsequently ~~discovered~~ <sup>discovered</sup> the ~~same~~ <sup>same</sup> ~~process~~ <sup>process</sup> in the cases of mannitol and dulcitol, and obtained isobutyl iodide. The investigations of Ecker ~~on~~ <sup>on</sup> the higher alcohols ~~produced~~ <sup>produced</sup> during alcoholic fermentation yielded the important proof that these alcohols do not belong to the normal series. He showed that fermentation "butyl alcohol" is converted by oxidation into isobutyraldehyde and isobutyric acid, and was able to synthesise the latter from isobutyl iodide by conversion into the cyanide and subsequent hydrolysis.

Other researches which may be mentioned are the isolation of glycolic acid from unripe grapes (with Hoster, 1864); the synthesis of sodium oxalate by the action of heat on sodium formate (1868); the study of the conditions under which ether is hydrolysed to alcohol (with Fischer, 1868); the synthesis of phenyl-lactic acid (1880); the preparation of pyruvic acid by the distillation of tartaric acid (1881); and the formation of carbostyryl from quinoline (1882).

The ~~researches~~ <sup>researches</sup> in the aromatic series include an important series of papers on the isomerism of the cinnamic acids, and also an interesting paper published in 1882, in conjunction with Lapp, on the synthesis of tyrosine from phenylalanine.

In 1875 ~~Beckmann~~ <sup>Beckmann</sup> carried out (with Widmann) an important investigation on the nitration of benzoic acid, in which he definitely disproved Fischer's statement that more than three nitrobenzoic acids exist. He was also able to disprove, in a series of very careful investigations carried out in conjunction with Kaper, F. Fischer, and Lapp, the statement of Wislicenus (1863) that the lactic acid produced from the product of the action of potassium cyanide on ethylene chlorohydrin, and also contained in small quantities in meat extract, is different from the hydracrylic acid obtained by ~~Beckmann~~ <sup>Beckmann</sup> from  $\beta$ -iodopropionic acid.

W. H. P.

### RUDOLPH FITTIG.

BORN DECEMBER 6TH, 1835; DIED NOVEMBER 19TH, 1910.

RUDOLPH FITTIG, who died somewhat unexpectedly in November 1910, was born in Hamburg in 1835. He was a student under Limpricht at Göttingen, becoming "Privatdocent" in the University in 1860 and honorary professor in 1866. In 1870 he was appointed professor in the University of Tübingen, and transferred in 1876 to the University of Strasburg as successor of A. Baeyer. As professor and director of the Chemical Institute

of this last University, he carried on with conspicuous success to the end of his life the teaching and research for which this Institute has become so generally renowned in the scientific world. It is of interest to add that during his early life at Göttingen he served for a short time as assistant to Wöhler.

Fittig's originality as an investigator became manifest at the beginning of his career. The well-known synthetical process for preparing the homologous hydrocarbons of the benzene series by the action of sodium on a mixture of the haloid derivatives containing the required radicles was his first important contribution to organic chemistry. The researches which laid the foundation of this still valuable method commenced as far back as 1862 with the discovery that diphenyl was formed by the action of sodium on monobromobenzene. The further developments of this work in the direction of determining the constitution of the isomeric hydrocarbons by means of the products obtained by the successive oxidation of the side-chains have become so intimately incorporated into our modern text-books that their authorship is apt to be overlooked by the modern student. Among his early discoveries must also be included the hydrocarbon phenanthrene, which was isolated from coal tar and characterised about the same time (1872) by Griess and by Fittig and Ostermayer.

Another line of work with which Fittig's name will be always associated is that exhaustive series of researches upon unsaturated acids and lactones which he commenced in 1873 with Ira Remsen, and which were continued with various colleagues for over twenty years. A summary of this work was given before the German Chemical Society in 1894. Here again he enriched chemical science by a succession of discoveries which have now become common knowledge, and the lecturer who discourses before his class about the complicated isomeric relationships between itaconic, citracohic, and mesaconic acids and their derivatives is really giving an account of Fittig's results. Of this work certain developments stand out conspicuously, notably the synthesis of coumarone from coumarin (Fittig and Ebert, *Annalen*, 1882, 216, 168), the preparation of the complete set of six optically active and inactive modifications of phenylparaconic acid commenced in 1882 (Fittig and Jayne, *ibid.*, 108), and, above all, the synthesis of  $\alpha$ -naphthol from phenylisocrotonic acid, which at the time of its announcement was at once recognised as a discovery of the first order of importance in connexion with the question of the constitution of naphthalene derivatives (Fittig and Erdmann, *Ber.*, 1883, 16, 43; *Annalen*, 1885, 227, 242).

It would be impossible to do full justice to the immense array







*Hans Lindell*

of discovery for which we are indebted to Fittig within the compass of this notice. His work is characterised generally by the substantial body of experimental evidence on which his conclusions are based. In theoretical matters he did not display much speculativeness, and yet one of his suggestions has turned out to be one of the most prolific sources of formula reconstruction among cyclic compounds ever introduced into organic chemistry. It was Fittig who, in 1873, first showed that the formula of benzoquinone might be written on the double ketonic type by making the phenylene residue of the benzene ring quadrivalent instead of bivalent, as in the earlier "peroxide" formula of Graebe. The so-called "quinonoid" structure, which is now so liberally assigned to all sorts of aromatic compounds, is in fact Fittig's "ketonoid" conception applied to particular cases.

In addition to his original papers Fittig contributed to general chemical literature the "*Grundriss der organischen Chemie*" (1872; 11th ed., 1886-87), and he edited the revised edition of Wöhler's "*Grundriss der organischen Chemie*" (10th ed., 1877). He collaborated with Beilstein and Hübner in editing the new series (1865-1871) of the *Zeitschrift für Chemie*, and from 1895 he was one of the editorial staff of Liebig's *Annalen*.

R. M.

#### HANS HEINRICH LANDOLT.\*

BORN DECEMBER 5TH, 1831; DIED MARCH 15TH, 1910.

On the 15th of March, 1910, died one of the oldest members of the present generation of chemists, the patriarch of physical chemistry, Hans Heinrich Landolt. He was born on the 5th of December, 1831, in Zurich, and had thus reached the ripe age of seventy-eight years, having enjoyed the good fortune of not having outlived himself. He will remain in the memory of his scientific colleagues and in the hearts of his friends and relatives as active and full of life to the end.

"Landolt was a scion of the old and respected patrician family of Zurich, to which belonged Salomon Landolt, whom Gottfried Keller has portrayed so admirably in his 'Züricher Novellen' as 'Der Landvogt von Greifensee.' This ancestry was unmistakably evident in his entire personality: simple and upright, homely, and yet full of native dignity, free in thought, feeling, and action, entirely without any religious or political superstition, Landolt was the prototype of the free and sturdy Swiss citizen." These

\* Adapted from the obituary address by the late Professor J. H. van't Hoff (*Sitzungsber. K. Akad. Wiss. Berlin*, 1910).

admirable words of his lifelong fellow-worker, Professor Brühl, may serve to introduce the portrait of our universally respected and beloved foreign Fellow.

Landolt's early life in Zurich was happy and free from care. He was industrious, even as a child, and soon displayed his scientific proclivities by devoting himself passionately, at the cost of his grandparents' carpets and curtains, to chemical experiments and fireworks; flame and light were destined on many later occasions to play a prominent part in his more serious researches.

At the age of nineteen Landolt entered the University of his native town for the study of chemistry and physics, attending the lectures of Löwig; and in the same year his first work, on "Stibmethyl," appeared in the "Schriften der Naturforschenden Gesellschaft" in Zurich. Shortly afterwards appointed assistant to Löwig, he followed him in 1853 to Breslau, for owing to his parents' decease, his ties to his native land were loosened; nevertheless, he kept in touch with the town of his birth, and maintained personal relations with his numerous friends by annual visits.

Before Landolt settled, he filled appointments in Berlin and Heidelberg, and again for a short period in Breslau.

At first, in 1853, while still in Breslau under his chief Löwig, he obtained the degree of Doctor of Philosophy on the strength of a dissertation, "Ueber die Arsenäthyle." This research, arising directly from his first work, proved of great importance to the law of valency. Then followed his journey to Berlin, the chief cause of which was the presence of Mitscherlich, Rose, Johannes Müller, and Dubois, whose lectures he attended. Facilities for experimental research in a chemical laboratory were, however, at that time practically non-existent in Berlin; he therefore left for Heidelberg, where Bunsen, whose personality had attracted Landolt whilst he was still in Breslau, had just commenced work in a newly-founded institute.

His experience in Heidelberg, and especially Bunsen's influence, had a great effect on the direction of Landolt's development, and he loved to dwell on the recollection of those times and on Bunsen's character, which was in many respects akin to his own.

He lived together with von Pebal in the Meierei near the old chemical laboratory in the Hauptstrasse. To the common dinner table at the Bayrische Hof came, among others, Lothar Meyer, August Kekulé, Beilstein, Bahr (subsequently assistant-professor in Upsala), Frapolli (afterwards in Milan), Pavesi (later in Pavia), Goupillat (afterwards in Sèvres), and also Adolf Wagner, of Berlin.

Landolt and Quinke used to work together in the new institute in the small gas-room with two benches.

After devoting himself for a short time to the electrolytic production of calcium and lithium, Landolt started an investigation of the gases produced in the Bunsen burner, which had been constructed in the winter 1854-55. Association with Quinke in work, as well as in frequent week-end excursions into the surrounding country, resulted in a friendship which was severed only by death.

In 1856 Landolt returned to Breslau, where he was soon afterwards joined by Lothar Meyer and Beilstein, and in the same year he became a lecturer in chemistry on the strength of his monograph on "*Chemische Vorgänge in der Flamme der Leuchtgase*."

In the year 1857, at the early age of twenty-six, he was called from Breslau to Bonn, being the youngest "*Extraordinarius*" in Prussia. Chemistry was there represented at that time by Bischof, the chief professor of chemistry and technology, and by Baumert; pharmacology by Bergemann. With all of these Landolt, soon entered into cordial relations. Other members of his circle of friends at Bonn were Usener, Schönfeld, Pflüger, and subsequently Bettendorf, who was Landolt's assistant for some time, as well as Horstmann, his pupil, collaborator, and life-long friend. In his new position Landolt commenced his great and fundamental researches on the influence of the atomic composition of liquids containing carbon, hydrogen, and oxygen on the transmission of light; they were published during the years 1862 to 1864 in Poggen-dorf's *Annalen*, and were largely stimulated by Pflüger, one of Landolt's many friends in Bonn, as well as by the mathematician and physicist Beer. These investigations were a continuation of the previous researches of Gladstone and Dale, but championed in particular the new points of view opened out by the laws of constitution, then in process of formulation, which finally rendered possible the calculation of the refractive power of the chemical molecule from the refractivities of its constituent atoms, by taking into consideration the manner in which these are linked together. Landolt in later years undertook the solution of many of the problems raised by these magnificent researches of his youth. For after the notable investigations of Hertz (1887-1888) had demonstrated the identity of optical and electric propagation, and had shown that light waves are differentiated from electric waves merely by vast difference in size, Landolt (1892), in collaboration with Jahn, again took up his former line of work, determining the molecular refractivity of organic substances for rays of very great wave-length, that is, electric waves. In general, relations were

found similar to those of light-rays, with, however, several remarkable differences which remain as yet incompletely explained.

At Bonn, in 1859, Landolt began at an early age his happy family life by marrying Milla Schallenberg, the amiable and beautiful daughter of Swiss parents settled in Bonn.

On Bischof's resignation August Wilhelm Hofmann was called from London to Bonn, where, as the result of his urgent representations, the most extensive chemical institute in the world at that time was erected. But before the building was completed, Hofmann had accepted a chair in Berlin, his place at Bonn being taken by August Kekulé, who came from Ghent. To him and to Landolt, who was appointed to a full professorship, and who had meanwhile completed his classic research on the vapour-pressure of homologous compounds, was assigned in 1867 the direction of the new institute, and these two men, occupied in totally different spheres of scientific activity, worked in complete harmony in the administration of their laboratory. As early as the year 1869 Landolt was appointed to the head of the newly-founded technical college at Aix-la-Chapelle, where a stately chemical institute was built according to his plans.

The time spent in Bonn remained in Landolt's memory as the most pleasant period of his life, and in his last years he entertained serious thoughts of retiring to that town. This plan, however, was not carried out, although he selected Bonn as his last resting-place.

Landolt's first task in Aix-la-Chapelle was the erection of the new institute, in which work he had the help of his assistant, the late Professor Brühl. The very best was aimed at, with perhaps exaggerated detail, for it is impossible to deny that, to a casual visitor, the building appears unnecessarily complicated. On the other hand, many novel and useful arrangements were installed, for example, an electrically illuminated projecting-lantern was introduced by Landolt in his theatre, and at once became an indispensable aid to demonstration.

Landolt's investigations were carried out from the point of view characteristic of the physical chemistry of that period: the relations between physical properties and chemical constitution. In accordance, however, with the more practical side of a technical college, polarised light, which is of great importance in the sugar and other industries, was now accorded especial attention. Ample success crowned his efforts. His admirable researches ("Ueber das Vermögen organischer Körper, das polarisierte Licht zu drehen") exhausted the entire field; Landolt made his name famous throughout the world of science and technology by his classical experimental

work on this subject, by improvements and novel designs in polarimeters, as well as by his standard book on "Das optische Drehungsvermögen organischer Substanzen" (1879); the second edition of this work, prepared by him in 1898, is even to-day unquestionably a classic, and a most exhaustive and trustworthy compendium of polarimetry. Of his scientific achievements in this field, the most prominent is the law, which will undoubtedly remain for ever associated with his name, that the rotation of salts of active acids and bases in aqueous solution may be calculated from constants corresponding with each acid or base, and is independent of the nature of the salt. Stereochemistry, moreover, is indebted to Landolt for vigorous aid at its rather difficult birth, through the support of its laws by his undisputed authority in the domain of optical activity.

These purely scientific achievements gained the respectful attention of representatives of the law, of technical industries, and even of agriculture, owing to the fact that the polarimeter, in conjunction with Landolt's measurements of optical rotatory power, plays so considerable a part in analysis and standardisation in the manufacture of sugar, alkaloids, terpenes, camphor, and scents. Wherever an industry begins to develop, a collector of excise is certain to be close at hand. It has thus come about that the name of Landolt is known to customs officers, and even to agriculturists, with whom he certainly had otherwise but little in common. For the same reason, also, Landolt was called in 1880 by the Prussian Ministry of Agriculture to the newly-founded Agricultural College in Berlin, where he remained until the year 1891.

At the Agricultural College he was again called upon to construct and reconstruct his laboratories, collaborating during these years with Dr. Börnstein in the compilation of the well-known "Physikalisch-chemischen Tabellen," the preparation of which was distinguished by the greatest care and accuracy. The third edition, brought out in 1905 with the assistance of Professor Meyerhoffer, and generously subsidised by the Berlin Academy of Sciences, is of so indispensable a nature that a project has been advanced by the International Congress of Applied Chemistry for an international committee to publish periodical editions of tables of this character.

In the year 1882 Landolt became a member of the Berlin Academy. To this period are to be ascribed the highly remarkable investigations into the velocity of the reaction between iodic acid and sulphurous acid (*Sitzungsber. K. Akad. Wiss. Berlin*, 1885--1886). This reaction, the mathematical calculation of which, attractive as the problem is, has remained unsolved to the present

day, is one of those in which the time-period is most accurately determinable in advance from experimental data.

In 1891 Landolt was appointed, as successor to Karl Rammelsberg, director of the second chemical institute of the Berlin University. This position he occupied until his retirement from active life in 1905, an occasion on which he was awarded the Great Gold Medal for Science and Art. His experimental work at this period bears, in a marked degree, the stamp of infinite patience, and is directed less towards the acquisition of new points of view and of new methods than that previously referred to.

The series of investigations was opened by a number of most careful determinations of melting points, large quantities of the substances under examination being prepared in the highest possible degree of purity. The results obtained were connected with the determination of molecular weight, the importance of melting points in this respect having gradually become recognised. Then followed a series of investigations relating to the problem whether crystalline substances could by extreme comminution be deprived of their crystalline structure. An ingenious suggestion—that the optical activity of sodium chlorate in the crystalline form could be traced from step to step—permitted this question to be definitely decided in the negative. It is evident that the state of division obtained in those preparations did not remotely approach the possibility of separating molecule from molecule.

The third, last, and perhaps most remarkable series of investigations related to the question of the possibility of change in weight during chemical reactions. This problem, which had been dealt with by Lavoisier in the first half, and by Stas in the second half of the nineteenth century, was now, with the aid of the most perfect apparatus, again taken up, and was continued for over ten years. The re-examination of the facts, which, as is well known, led to a negative result, was carried out most opportunely, immediately preceding as it did the discovery of the altogether unexpected phenomena of radium which appeared to assail the fundamental laws of experimental science.

We may form some idea of the devotion required by these accurate experiments of Landolt when we consider the expenditure of time which they involved. But in addition to the question of mere perseverance, there was much that would deter the majority of investigators from undertaking such a work; the quarter of Berlin in which Landolt's institute was situated afforded the freedom from earth-tremors requisite for such delicate weighings only twice in the twenty-four hours: once at noon, and again in the small hours of the morning. To carry out a two-hours' weighing in such circumstances is not a task to be relished.

The work he gave to posterity will remain of monumental importance. It was of no small advantage that the final experiments were carried out, after Landolt's retirement, in the Government technical-physical laboratories of which he was curator. Indeed, another important research was planned in collaboration with Quincke, but this was never put in hand. The minor experiments connected with the indestructibility of matter, which refuted the statement of Zengels that glass was permeable to iodine and similar substances, completed Landolt's life-work. His last scientific communication was but recently read before the Royal Prussian Academy of Sciences, whilst for the following May he had contemplated writing a comprehensive report on the determination of weight.

Landolt's temperament was a most peculiar one, dominated by a modest and delicate, although irresistible humour. This, which in others is frequently only the result of wide experience in life, was in him certainly innate, for Roscoe described him, as early as the Heidelberg days (1865), as "full of dry humour, aber etwas schweigsam," commending at the same time his good-natured equability in the discussion of scientific matters. This humour was always deep, and could be personal, but never wounded; indeed, Landolt never hesitated to turn the point of his wit against himself, although always with that discrimination which may be regarded as characteristic of him.

Professor Stumpf once described Landolt as "ein Lebensphilosoph," and this is a true characterisation, both in a scientific and a personal sense. Although in neither respect was he spared suffering, he always took the cheerful view of a true philosopher. Fundamentally, his character was serious, yet he knew so well how to take this serious view of life that he rarely appeared grave, and never lost the subtle smile which was one of his leading characteristics, and which won the hearts of all. One might have thought that there was for Landolt but one all-important thing in life: his cigar. The following anecdote, relating to his last years, is told by his widow: The secretary of the Berlin Academy, Professor Diels, not long ago sent to Landolt a birthday greeting, expressing the hope that he might be as fresh on his eightieth birthday as he was then. Landolt went at once to his desk and penned the following reply:

"Die freundlich gewünschten 80  
Will in Geduld ich erharren,  
Ich hoffe die Sache macht sich  
Vermittels recht vieler Zigarren."

He hoped, indeed, to do many another piece of work, and was also considering Ostwald's suggestion that he should write down reminiscences of his life. It is a pity that he was unable to do



this, for, in view of his constant good humour, his clear and simple conception of life, his kindness and thoughtfulness for others, and his large circle of acquaintances, these would have proved interesting memoirs.

Landolt's was essentially a robust nature. He had lived long, and accomplished much without appreciable disturbance in his health. As recently as last year he was planning with Quincke a research of considerable extent. But after recovering from an attack of pleurisy at Karlsbad, he suffered from shortness of breath. The experiments planned with Quincke were never carried out, as their prospects appeared somewhat uncertain. Landolt soon thereafter made over all his apparatus to his son and to his grandson, and gave up experimental work altogether.

On the afternoon of Monday, March 7th, a week before his death, after Landolt had worked uninterruptedly from half-past nine until two o'clock, he was attacked by a fit of choking, which recurred in the evening. The doctor at once predicted the worst. The painful attacks were repeated; the action of the heart and kidneys failed, poisoning his strong system, which was racked with pain in spite of repeated doses of morphia. These were days of torture and anxiety. He lamented that it should be necessary to go through so much suffering in order to die, but he frequently refused the injection of morphia in order to be able to talk over with his youngest grandson, Erich Liebreich, the unfinished portions of his work. He dictated some sentences; explained in which pigeon-holes of his desk were to be found his manuscript and notes—but soon relapsed into unconsciousness. He died at three o'clock on the morning of March 15th.

Landolt was buried, in accordance with his desire, at Bonn, where he had held his first position as a teacher, and had found his life's companion.

H. T. C.

#### NIKOLAI ALEXANDROVITSCH MENSCHUTKIN.

BORN OCTOBER 25TH, 1842; DIED FEBRUARY 5TH, 1907.

THE year 1907 will ever be memorable in the annals of chemistry on account of the losses, by the hand of death, in the ranks of our leaders: first, within three days of each other, Mendeleeff and Menschutkin in Russia, and only a few weeks later in France, Moissan and Berthelot.

The name of Menschutkin was familiar enough in England, and his services to science, principally in the domain of physico-organic chemistry, were recognised by the Chemical Society in 1898, when





it was added to the limited list of Honorary and Foreign Members, but his figure was less known in this country than that of his great contemporary Mendeléeff. He was, however, present at the famous meeting of the British Association in Manchester in 1887.

The story of Menshutkin's life has been written by his son and successor in the Polytechnic Institute of St. Petersburg-Sosnowka, Professor Boris N. Menshutkin. Unfortunately, it appears in the Journal of the Russian Chemical Society only in the Russian language, and is therefore inaccessible to the majority of chemists, but the facts relating to the greater part of Menshutkin's scientific work are available for English readers through the medium of the abstracts which have appeared since 1871 in the Journal of the Chemical Society. His book on analytical chemistry has also been extensively used in England and America in the form of the English translation by James Locke.

\* Nikolai Alexandrovitch Menshutkin was the sixth son of his father, Alexander Nikolaevitch Menshutkin, a member of a family, chiefly of merchants, long established in St. Petersburg. His education was received, first at the Gymnasium, which he left, in December, 1857, with the highest distinction, in order to proceed to the University. As he was still under the prescribed age of sixteen years, it was only in the autumn of 1858, and then by special favour, that he was able to enter as a student in the natural science division of the Physico-mathematical Faculty of the University. During three years he worked diligently until, in the autumn of 1861, he experienced, for the first but not the only time, the effects of the operation of those administrative agencies which are the bane of intellectual life in Russia. In consequence of some disturbance among the students, probably of a political character but also probably of no importance, Menshutkin and thirty-one other students were "sent down."

However, in the spring of the following year he succeeded in passing the final examination, and attained the degree equivalent to Ph.D. During the latter part of his course his attention was specially directed to chemistry, which he studied under Professors Wokkressenski, Mendeléeff, and Sokoloff. He thus acquired a sufficient knowledge of theory, but he was unable to work practically, as at that time the entire laboratory of the University consisted of only two small rooms. In order to obtain the necessary practice he therefore had to go abroad, and in the following three years he spent two semesters with Strecker in Tübingen, a

\* The writer is indebted for the facts narrated in the following account to the notice which appears in *Ber.*, 1907, 40, 5087

year (1864-5) with A. Wurtz in Paris, and a semester in the laboratory of Kolbe in Marburg.

In the meantime, many changes were introduced into the constitution of the Russian universities. In 1863 the universities obtained academic freedom, they chose for themselves the professors, deans, and rectors, at the same time the number of professors was increased, the means of teaching improved, and, especially owing to Mendeléeff's efforts, the laboratory at St. Petersburg was enlarged.

In 1865 Menshutkin's return to St. Petersburg prevented his dissertation, which had already appeared in the *Comptes Rendus* of the French Academy under the title "Action du chlorure d'acétyle sur l'acide phosphoreux," and in March, 1866, obtained the degree of Master in Chemistry, together with the "venia legendi." Thereupon he began in the autumn a course of lectures on organic nitrogen compounds, and worked at his dissertation for the Doctorate. Having been appointed "Docent" in Analytical Chemistry, he began, in the enlarged laboratory, the course of instruction in that subject which he continued to direct for seventeen years down to 1885.

Early in 1869 the dissertation was ready, the subject being "The Synthesis and Properties of the Ureides," and on the 6th April Menshutkin became Doctor in Chemistry, and thereby eligible for a professorship.

At that time the two chairs of pure chemistry and organic chemistry were occupied by Mendeléeff and Butleroff respectively. The third, relating to technical chemistry, was unoccupied, and in the exercise of the powers recently conferred by the Government, the University Council decided to associate the vacant post with analytical chemistry. Menshutkin was appointed, and although officially Professor of Technical Chemistry he was actually Professor of Analytical Chemistry. In connexion with his teaching he then proceeded to rearrange the course of instruction, and in 1871 he brought out his well-known text-book. This has passed through nine editions, and has been translated into German and English. This work is well and clearly written, and although it contains nothing new in the methods of analysis described, the course represented is an excellent one for students. The author's views as to the place of analytical chemistry in the curriculum, and its relations to other departments of scientific chemistry, are set forth in the preface, from which the following extract will be sufficient. He says: "The student cannot rightly turn to analytical chemistry until he has obtained a thorough preparation in the general science; and his knowledge of the latter is measured

not by the number of single and isolated facts with which he is familiar, but by the clearness with which he understands the fundamental chemical phenomena and theories. For these reasons I strongly advise the beginner not to devote himself too quickly to analytical chemistry. . . . If the above conclusions are correct, the practice of chemical analysis must be pursued in the same way as purely scientific investigations. The chemist proves the correctness of an induction in the latter by means of suitable experiment, in obtaining the best possible conditions for which he must be governed by analogy. The same method of procedure should be adopted by the analytical student, in continually proposing questions to himself and answering them by properly selected experiments." With these remarks most experienced teachers will be in hearty agreement.

In the year 1871 Menshutkin became Secretary of the Physico-mathematical Faculty, and in 1879 he was appointed Dean, an office which he held until 1887.

The assassination of the Emperor Alexander II. in 1881 was followed by the adoption of severe repressive measures, from the effects of which the universities, with all the other institutions in the country, suffered in many ways. The autonomy granted in 1863 was revoked, and the officials, including professors, could only be appointed by the Minister of Public Instruction, the students were required to resume the uniform of 1835, the admission of students rendered much more difficult, as they could only be received from certain gymnasia, the fees were raised considerably, and the number of professorships reduced. In chemistry two only remained, namely, the chairs of pure and technical chemistry.

Naturally, professors and students alike were discontented with this state of things, and in the years 1887-8 serious disturbances occurred. These were followed by the resignation of the rector and several other officials. Butleroff having resigned his post in 1885, Menshutkin had to take up the teaching of organic chemistry, in addition to his other duties. About this time he prepared his large handbook of organic chemistry, which appeared in three successive editions, and in 1888 he published a history of the development of chemical theory. As both these books were written in the Russian language and were not translated into any other, they remain practically unknown to foreigners.

One of Menshutkin's most serious undertakings was the building of the new chemical laboratories of the University. Although the old laboratory had been from time to time enlarged, it was very inconvenient and dark. As it was also far too small for the

number of students desiring admission, a new laboratory was granted on the petition of Mendeléeff and Menschutkin. It was, however, only in 1890 that the money could be found and the plans prepared, and in this year Mendeléeff resigned his chair. This retirement left Menschutkin in the position of senior Professor and Chairman of the Building Committee. After visiting, in company with the architect, Krassowski, several of the chief continental laboratories, Menschutkin returned to St. Petersburg, and the work proceeded so rapidly that the new laboratory was ready for occupation in October, 1894.

In this laboratory Menschutkin worked eight years, teaching only organic chemistry. The later years, however, from 1899 onward, were much disturbed owing to frequent disorders among the students, in consequence of which, from 1899 to 1906, the lecture courses were never completed. In 1902 Menschutkin was transferred to the new Polytechnic Institute, about 6 kilometres north of St. Petersburg, in the district Sosnowka, while still retaining the Professorship of Organic Chemistry in the University, and delivering lectures in that subject. Here he exercised the functions of Professor of Analytical and Organic Chemistry, as well as Dean of the Mining Division. To these offices were added the business connected with the Russian Chemical Society, of which Menschutkin had been Secretary from the commencement down to 1891, and of which he continued to hold the Editorship of the Journal until 1901. In 1906 he was elected President of the Society.

Nor was his activity confined to academic spheres. As deputy of a province he was able to take part in the discussion of questions relating to popular education, and many new schools owe their existence to his exertions. He was also President of the Committee on the establishment of an Agricultural Institute at St. Petersburg.

In his political views he belonged to the Opposition. He often visited the University during the periods of most severe reaction, and in the Council of the Polytechnic he was bold enough to express the view that academic life could only develop under the condition of civil political freedom, and succeeded in carrying a resolution to that effect. He was one of the founders of the Academic League (Bund), and at the end of 1905 he took an active part in the elections for the first Duma. He was one of the founders of the party of democratic reform.

Menschutkin had suffered for many years from disorder of the kidneys, and at the end of 1906 he had an attack which, however, had apparently passed off. His death, which occurred in

the early morning of the 5th February, 1907, was sudden and unexpected.

As to Menshutkin's scientific work, his earliest efforts have been already mentioned. His principal systematic researches relate exclusively to the study of organic compounds from the physical point of view. His important memoirs on the influence of isomerism among alcohols and acids on esterification may be read in full abstract in the *Berichte D. Chem. Ges.* (Bd. 10, 11, 13, 14, 15, 16). Many years earlier it had already been shown by Berthelot and Péan de St. Gilles that in the interaction of acids and primary alcohols there is a limit, both to the rate of change and the amount of ester formed. These researches belong, however, to a time before the complete recognition of isomerism among the alcohols. Menshutkin, in a long series of experiments, showed that, both in respect of rate and limit, the primary, secondary, and tertiary alcohols differ from one another, and that unsaturated differ from saturated alcohols. The molecular weight of the alcohol concerned has also a considerable influence on the result, the limit rising generally with molecular weight, although the rate is diminished. The first series of experiments were made with acetic acid and various alcohols; the succeeding memoirs included the results of work with a variety of acids. Subsequently the rate of chemical change was studied in the case of the formation of amides and anilides by the action of ammonia and aniline on acids by means of the same method as was employed in the esterification experiments. Here again the influence of isomeric differences was equally manifest. These researches led on to others, such as the study of the mutual displacement of bases in homogeneous systems, and the influence of temperature on the rate of several reactions. Abstracts of all the memoirs relating to these researches are provided in the Journal of the Chemical Society.

Menshutkin's researches, from 1889 to 1895, were devoted to the study chiefly of the amines and of the velocity of their interaction with alkyl halogen compounds, and the influence of isomerism on the rate of change. In this connexion the interesting fact was discovered that so-called "indifferent" solvents exercise a quite extraordinary influence on the rate of the reaction.

Continuing these investigations down to the end of his life, Menshutkin succeeded in establishing a large number of other facts connecting together constitution or structure and chemical activity, as well as physical properties, such as boiling point, melting point, and specific gravity. He must, in fact, be regarded as one of the chief pioneers in the difficult study of chemical



dynamics, for although Berthelot had been before him in observations of the rate of esterification, and Harcourt and Esson, in 1864, had made a bold beginning in another direction, the material requisite for generalisation was wanting until much of it was supplied by the continuous, steadfast, and careful researches of the Russian chemist.

In reviewing the career of a great man, interest and sympathy are roused as much by a consideration of the difficulties he has had to encounter and the influence they may be supposed to have had on his character, and the position he ultimately reached, as by any record of his successes or times of triumph. In many cases, these difficulties occur in early life, and among the worst may be reckoned poverty, ill-health, want of education, or want of friends. These are disadvantages which may beset the youth of any nation, although it may sometimes be said that there are uses in such adversity,

" Which, like the toad, ugly and venomous,  
Wears yet a precious jewel in his head."

The difficulties which haunt the Russian man of science are not specially of this kind; they do not belong to his youth only or to the circumstances surrounding him individually. They follow him through life, they belong to the atmosphere in which he draws his breath, and over which he has usually no power or control. Those who live under other skies cannot but look wistfully across the frontier of this great country with sympathy in their hearts, and with admiration for those who, like Menschutkin, have succeeded, in the face of disturbance and of official discouragement, in bearing a distinguished part in building the foundations of modern science.

W. A. T.

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## ERRATA.

### COLLECTIVE INDEX, 1893-1902.

#### PART II. SUBJECTS.

Page	Col.	Line.
605	ii	8* <i>delete</i> "(isoinazole)."
605	ii	5, 6* " (GABRIEL and NEUMANN), 1893, A., i, 348.
834	i	20* " "See 2:5-Diphenylpyrazine."
834	i	20* <i>insert</i> " (GABRIEL and NEUMANN), 1893, A., i, 346."

#### VOL. XCIV (ABSTR., 1908).

##### PART I.

	Line.	
762	1*	} for "cinnamylideneacetophenonehydroxylamine" read "hydroxyl-aminocinnamylideneacetophenoneoxime."
763	10	

#### VOL. XCIX (TRANS., 1911).

810	17*	for "an acid salt, $C_6H_3O_5CuH$ " read "a double salt, $C_6H_3O_5CuK$ ."
810	15*	" "protocatechuate" read "pyrotartrate."
810	14*	" "pyrotartrate and malate" read "protocatechuate and maleate."
810	13*	" " $C_2$ " read " $C_6$ ."
1545	4	" "39.4" read "32.4."

#### VOL. C (ABSTR., 1911).

i, 597	3	for "GRISCHKWITSCH-FROCHIMOWSKY" read "GRISCHKWITSCH-TROCHIMOWSKY."
i, 687	8*	" "O $\begin{array}{c} \diagup \text{CO} \cdot \text{C} \cdot \text{N} \cdot \text{C} = \text{CR} \\ \diagdown \text{N} = \text{CPh} \text{CMe} \cdot \text{N} \end{array}$ NR' " read
		"O $\begin{array}{c} \diagup \text{CO} \cdot \text{C} \cdot \text{N} \cdot \text{C} = \text{CR} \\ \diagdown \text{N} = \text{CPh} \text{NMe} \cdot \text{N} \end{array}$ CR'."
i, 687	3*	" "NMe <sup>o</sup> CMe $\begin{array}{c} \diagup \text{C} \cdot \text{N} \cdot \text{C} \\ \diagdown \text{NPh} \cdot \text{CO} \end{array}$ CO <sup>o</sup> NH $\begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CO} \cdot \text{NH} \end{array}$ " read
		" "NMe <sup>o</sup> CMe $\begin{array}{c} \diagup \text{C} \cdot \text{N} \cdot \text{C} \\ \diagdown \text{NPh} \cdot \text{CO} \end{array}$ CO <sup>o</sup> NH $\begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CO} \cdot \text{NH} \end{array}$ " "
ii, 567	21, 22	" "remain in the disintegration, of which" read "remain, in the disintegration of which."
ii, 570	4	" "than" read "that."
ii, 703	5	" "21" read "22."

\* From bottom.



**SIR WALTER PALMER, BART.**

BORN FEBRUARY 4TH, 1858; DIED APRIL 16TH, 1910.

By the death of Sir Walter Palmer we have lost one of the men whose value to the nation we are beginning to appreciate. As the third son of the late George Palmer, M.P. for Reading, the founder of the firm known all over the world as Messrs. Huntley and Palmers, he was one of the directors of a great commercial organisation. Owing to his father's foresight, and to his own natural bent, he received a thorough scientific education that enabled him to take his place on the board of directors as their natural scientific advisor, and out of the happy combination of commercial and scientific experience he developed an attitude of mind towards industrial problems and the scientific principles upon which modern industry must lean that made him an admirable example of the broad-minded captain of industry.

By inheritance and by the education of childhood and boyhood he was excellently endowed from the first. Issued, both on his father's side and on his mother's, from a long and healthy line of forbears belonging to the Society of Friends, his first education was sound and good. And, as a natural part of that education, he made early acquaintance with the outer world by travel and by the study of foreign languages. He matriculated at the age of seventeen at the University of London, and after three years of further study at University College and at the Sorbonne in Paris, he took his B.Sc.Lond., chemistry having been the subject to which he had devoted most attention.

He was now ready to enter upon the practical business of life, and went into the biscuit factory at Reading to serve as a "hand" in its various departments as the proper introduction to his service as a partner in the control and direction of the business.

In that capacity he worked actively for years, and applied his scientific knowledge and method to the technical improvement of biscuit-baking. He thus contributed largely to the commercial prosperity of the firm. As one step towards that end he was chiefly instrumental in the establishment of a chemical laboratory under the direction of a first-rate scientific chemist.

By his marriage in 1882 to Jean, daughter of W. T. Craig, M.P., Walter Palmer's natural disposition to take part in public life, and his natural taste for the literary and artistic aspects, were most happily seconded, and throughout their married life of twenty-seven years the natural generosity of husband and

wife were united, to the great benefit of many artists, and to the great enjoyment of a large circle of friends, both in Reading and in London.

In 1892 Walter Palmer took a leading part in the foundation of the University College of Reading, of which he was the first chairman, and of which the buildings were formally opened in 1898 by H.R.H. the Prince of Wales (King Edward VII.).

In 1891 he generously supported a scheme for the regular delivery of post-graduate lectures in physiology at the University of London, and provided funds for the equipment of the laboratory that was required for this purpose.

In 1898 he was returned to Parliament as the Unionist Member for the City of Salisbury. In 1904 he was created a baronet, and during the last few years until his death he served regularly as a member of the Senate of the University of London.

A. D. W.

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### CLXXXVII.—*The System: Palmitic Acid-Sodium Palmitate.*

By FREDERICK GEORGE DONNAN and ALBERT SIMPSON WHITE.

As a substance of very great commercial importance, soap claims a large share of attention from both the industrial and the academic chemist. Although the fundamental reaction—the saponification of an ester—is simple, and has been familiar for a great many years, there are processes in the manufacture of soaps, such as clear-boiling, salting out, etc., which are little understood from a scientific point of view.

Several papers have been published dealing with the condition of soaps in solution in various solvents, especially water (Krafft and collaborators, *Ber.*, 1894, **27**, 1747, 1755; 1895, **28**, 2573; 1896, **29**, 1328, 1334; Kahlenberg and Schreiner, *Zeitsch. physikal. Chem.*, 1898, **27**, 552; A. Smits, *ibid.*, 1903, **45**, 608; McBain and Taylor, *Ber.*, 1910, **43**, 321; *Zeitsch. physikal. Chem.*, 1911, **76**, 2, 179).

The conclusion was arrived at by Krafft that the formation of acid salts played no unimportant part in the chemistry of the soaps, and it was thought that an examination of the two-component system, fatty acid-sodium salt, would possibly afford confirmation of this view, and lead to the isolation of one or more acid salts.

Some preliminary measurements of the "initial freezing points" (called in future I.F.P.'s) of various mixtures of palmitic acid and

sodium palmitate had already been made in this laboratory by H. E. Potts, the results of which are given in the following table.

TABLE I.

No.	Sodium palmitate, per cent.	I.F.P.	No.	Sodium palmitate, per cent.	I.F.P.
1	0	60.65°	8	5	64.00°
2	1	60.50	9	10	66.50
3	2	60.15	10	15	68.60
4	3	60.00	11	20	70.70
5	4	60.70	12	30	75.80
6	5	61.60	13	40	88.70
7	10	65.20			

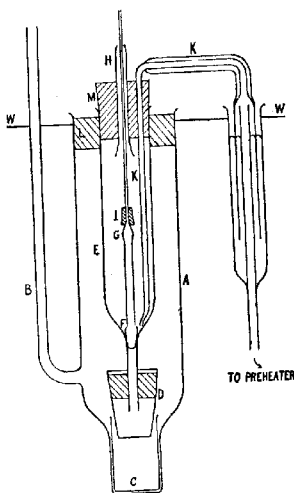
The results of experiments 1—7 were obtained by means of cooling curves. These gave very satisfactory figures when working with the pure acid, or with mixtures of low soap-content. At higher concentrations of the palmitate, however, they became very indefinite, and could not be repeated with any accuracy. The results of experiments 8—13 in table I. were obtained by a method of direct observation. The mixture was made up, melted, and thoroughly mixed, in a small, thin glass test-tube, which was then secured to the bulb of a thermometer by rubber bands, and dipped into a cooling bath. To prevent super-cooling, a stirrer of platinum wire was introduced, and this was lifted out at short intervals in order to allow a drop of the mixture to solidify on it, when it was reintroduced and vigorously agitated. The temperature at which a solid phase was seen to be formed was noted as the I.F.P. of that mixture.

Although no great accuracy can be claimed for these results, they show unmistakable signs of a eutectic at about 60°—a deduction which is corroborated by the appearance of a second halt at this temperature in some of the cooling curves. An attempt to redetermine these points with greater accuracy proved of no avail, as it was found that the mixtures had a very pronounced tendency to supercool, and that crystallisation was very slow, even when started. The viscosity also increases greatly with the addition of soap to the mixtures, at about 35 or 40 per cent. of sodium palmitate being very pronounced. Therefore, as these determinations of I.F.P.'s did not yield the data required with reference to the solid phases, no further time was spent on this work, but the isolation and examination of the solid and liquid phases in equilibrium with each other at various temperatures were proceeded with, the I.F.P. curve being used as a guide in fixing the temperatures and compositions to be used.

*Apparatus.*

The apparatus used in these solubility determinations consisted essentially of two parts, namely, an inner chamber where equilibrium was attained, and an outer case, for purposes of isothermal filtration. The whole is shown in Fig. 1, in which *A* is the outer case, which was plunged into a thermostat up to the level *WW*. A side-tube *B* led out of the thermostat to the filter pump, and the lower end of *A* was narrowed to accommodate a weighing bottle *C*, in which the liquid phase collected as it fell from a Gooch crucible

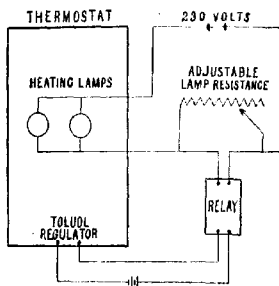
FIG. 1.



*D*, after having passed through a filter paper. *A* was closed at the top by a large cork, which was bored to support the equilibrium tube *E*, and was rendered air-tight by being covered with a layer of "plasticine," a patent modelling clay which was found very useful for such purposes. *E* was made of one-inch glass tube, narrowed off at the bottom, and sealed into a piece of narrow glass tube which passed through a rubber bung supporting *D*. Communication between *E* and *D* was cut off by means of a ground-glass plug *F*, the stem of which was enlarged into a small bulb *G*, and then drawn out on the upper side, in order to pass easily through the tube *H*, leaving a free air-outlet. A small cork *I* was

dropped on to *C*, the bottom end of *H* being enlarged to fit this cork, and so provide a means of supporting the stopper when lifted in order to allow the contents of *E* to flow down for filtration. The stirring was performed by means of a current of dry air, free from carbon dioxide, which was drawn through the mixture. This was admitted through a narrow glass tube *K*, drawn off to a fine jet at the lower end, and sucked out through *H*, which was connected to the filter pump. The end of the stem of *F* was cut off, so that when in position as shown in Fig. 1 there was a sufficient length projecting to afford a good hold for the fingers, and at the same time not too much to prevent a piece of pressure tubing being slipped over *H* without danger of breakage. When the stopper was raised for filtration it was no longer necessary to suck air out through *H*, which was then simply closed up by means of an

FIG. 2.



air-tight cap made of rubber tubing long enough to cover the stem in its new position. By this method air was prevented from entering the apparatus through *H* during filtration. Connexion between the equilibrium apparatus and the preheater—a thin glass spiral immersed in the thermostat, through which the air was passed after purification and before entering the apparatus—was made through mercury, so that the whole apparatus could be lifted easily, without damage to the fragile preheater, which was permanently mounted in the bath. The part of the inlet-tube *K* which projected out of the thermostat was made of thick-walled glass to minimise the temperature fall which must occur here.

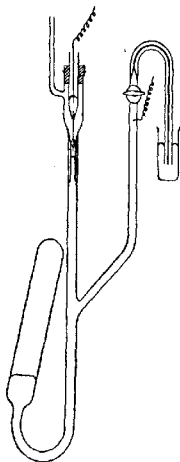
As, at the temperatures required, gas-heated thermostats have been found to be not very satisfactory, the bath used in this work was heated and controlled by electricity, and is perhaps worthy of a short description. Fig. 2 shows the connexions diagrammati-



cally. The heating lamps—two or three 250-watt radiator lamps, according to the temperature—were connected across the 230-volt mains through a relay, across the same terminals of which was also an external adjustable resistance of lamps. This arrangement had a two-fold advantage, since, besides reducing the sparking in the relay, it allowed the rate of cooling of the bath to be regulated. When the direct passage through the relay was broken, the current still had a path through this adjustable resistance in series with the heating lamps, which were thus always absorbing a certain amount of power. This point is of importance, as, at such high

temperatures, if the lamps are allowed to be quite extinguished, the cooling is so rapid that the fall of temperature cannot make itself readily enough felt through the walls of the regulator, and bad regulation results.

FIG. 3.



The regulator used was an ordinary toluene and mercury one, but was modified for the electric control, and also in order to allow the temperature to be varied over a considerable range with ease. As shown in Fig. 3, a side-tube was sealed on and bent upwards, having a glass tap just above the level of the thermostat. Above this a capillary tube made connexion with a mercury reservoir outside the bath, and a platinum wire was sealed in just below the tap. For the other contact a piece of stout platinum wire was sealed through the bottom of a narrow glass tube containing a little mercury, into which a copper wire could be dipped. This tube was passed

through a cork which fitted the enlarged top of the straight limb of the regulator, and the end of the platinum wire entered a piece of capillary tubing, being bent into the form of a spiral with a central point projecting downwards, in order to keep the contact between platinum and mercury rigidly in the centre of the capillary. To regulate to any desired temperature, mercury was poured into the straight limb until it began to flow over into the reservoir. It now syphoned over until the levels in the capillary and the reservoir were equal, and was ready for use. The detachable contact was put into place, and the bath heated up with the tap open until the temperature was approximately reached. The reservoir was now raised until the meniscus in the capillary was

nearly in contact with the platinum point, and the tap was closed.

If the temperature attained was not quite that required, the final adjustment was made by opening the tap, and either blowing or sucking down a side-tube sealed in to the straight limb for this purpose, and not by alteration of the position of the platinum contact, which was only made detachable for cleaning purposes. The regulator circuit was operated by an accumulator giving approximately 2 volts.

#### *Experimental Results.*

Using the I.F.P. curve as a guide, a mixture and temperature were selected which would, in all probability, give both phases in quantities sufficient for analytical purposes. This mixture was made up on a watch glass, and brushed into the apparatus. The cork *I* was then dropped into place, and the apparatus closed up by the rubber bung carrying *H* and *K*, which was pressed down firmly until quite air-tight. The temperature of the bath was adjusted, and if it was required to approach the equilibrium from the solid side the apparatus was at once put into the thermostat. In this case stirring was not started at once, as the powdery mixture would have been blown all over the apparatus. Sufficient time was therefore allowed for the acid to melt. The tube *H* was then connected to the filter pump, and a slow current of air drawn through. When it was desired to approach the equilibrium from the completely liquid side, the mixture was first melted by heating the apparatus in water until all the sodium palmitate had dissolved, and stirring was commenced immediately on transference to the bath. After having been maintained at this temperature for the desired length of time, the apparatus was lifted out and examined, to make sure that both phases were present in sufficient quantities. This could be done very easily and rapidly without fear of disturbing the equilibrium, as the whole apparatus was mounted on a single support, and was connected with the preheater through mercury, as mentioned previously. If the result of this examination was unsatisfactory, the apparatus was replaced, and the temperature altered in the required direction, and a further period allowed. If, however, both phases were present as desired, the apparatus was replaced quickly, and a short time allowed to neutralise the effect of the small amount of cooling that had taken place. The stopper was then raised, and *H* closed up as described, and the outlet tube *B* connected with the pump, thus sucking air through the solid phase collected in *D*, and allowing the liquid phase to fall into *C*. The phases so collected were then taken out,

and their sodium content estimated as sulphate, after careful ignition to drive off all the organic matter.

In order to gain a knowledge of the time necessary for the establishment of equilibrium, the following experiments were carried out at 60°.

TABLE II.

Condition of mixture before experiment.	Time in days.	Solid phase, sodium palmitate, per cent.	Liquid phase, sodium palmitate, per cent.
Liquid .....	2	22.84	19.1
" .....	2	22.84	19.22
" .....	2	22.95	19.1
Solid .....	2	22.84	19.33
" .....	2½	22.72	19.1
Liquid .....	2½		

From table II. equilibrium is seen to be sufficiently attained in two days, and as this was a convenient time, no further work was done on this question, but in the following experiments a period of at least two days was allowed for the attainment of equilibrium.

Table III. gives the results obtained, both in percentages of sodium and of sodium palmitate.

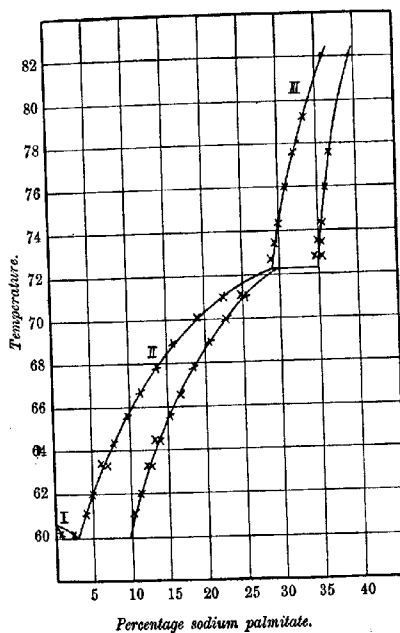
TABLE III.

No.	Temp.	Solid phase.		Liquid phase.	
		Per cent. Na.	Per cent. NaPa.	Per cent. Na.	Per cent. NaPa.
1	60.2°	0.06	0.7	0.19	2.3
1	60.2	0.05	0.6	0.19	2.3
2	61.1	0.84	10.20	0.32	3.97
2	61.1	0.85	10.30	0.34	4.17
3	62.0	0.92	11.12	0.41	4.96
3	62.0	0.93	11.34	0.41	4.96
4	63.3	1.02	12.33	0.54	6.53
4	63.3	1.05	12.81	0.52	6.28
5	64.4	1.14	13.78	0.66	7.98
5	64.4	1.12	13.54	—	—
6	65.6	1.28	15.47	0.82	9.91
6	65.6	—	—	0.82	9.91
7	66.85	1.38	16.68	0.95	11.48
7	66.85	1.32	15.95	1.00	12.09
8	67.75	1.55	18.73	1.12	13.54
8	67.75	1.545	18.67	1.15	13.90
9	68.95	1.70	20.55	1.37	15.56
9	68.95	1.71	20.67	—	—
10	70.00	1.89	22.84	1.59	19.22
10	70.00	1.89	22.84	1.58	19.10
11	71.00	2.10	25.38	1.87	22.60
11	71.00	2.07	25.02	1.87	22.60
12	72.9	2.90	35.05	2.37	28.65
12	72.9	2.85	34.45	2.36	28.52
13	73.5	2.65	32.39	2.42	29.25
13	73.5	2.68	32.03	2.45	29.37
14	73.5	2.90	35.05	2.39	28.89
14	73.5	2.93	35.41	2.37	28.65

No.	Temp.	Solid phase.		Liquid phase.	
		Per cent.	Per cent.	Per cent.	Per cent.
		Na.	NaPa.	Na.	NaPa.
15	74.4	2.98	35.41	2.48	29.98
15	74.4	2.91	35.17	2.48	29.98
16	76.0	2.97	35.90	2.54	30.70
16	76.0	3.00	36.26	2.53	30.58
17	77.6	3.02	36.50	2.65	32.03
17	77.6	—	—	2.65	32.03
17	77.6	—	—	2.76	33.36
18	79.2	2.95	35.66	—	—
18	79.2	3.00	36.26	—	—
18	79.2	3.00	36.26	2.98	36.02
19	82.0	3.28	39.64	2.97	35.90
19	82.0	—	—	—	—

The above results are shown graphically in Fig. 4. They are seen to form three pairs of curves, indicating the formation of three

FIG. 4.



series of solid solutions. The lower eutectic was already fixed by the second halt, noticed by Potts in his cooling curves. The second pair of curves appears to approach a maximum so nearly, before the second eutectic is reached, that further experiment was required to settle this point. An attempt was made to fix this second eutectic temperature also by means of cooling curves, but without result, on account of the supercooling and slow velocity of crystallisation mentioned before. The difficulty of obtaining definite results from cooling curves was found to increase rapidly with the addition of sodium palmitate to the mixtures, and with the compositions required for the present purpose the method was quite useless. The following two methods of obtaining the eutectic temperature by melting a mixture were therefore tried.

A mixture containing 29 per cent. of sodium palmitate and 71 per cent. of palmitic acid was melted and thoroughly mixed in a test-tube, and then cooled quickly. It was then allowed to remain in the thermostat for some time, after which it was examined, and its condition noted. The temperature was then raised slightly, and a further time allowed. This was repeated until two temperatures were obtained, at one of which the mixture was quite solid, and at the other partly liquid.

A 29 per cent. mixture was found to be quite solid at  $72.1^{\circ}$ , and partly liquid at  $72.6^{\circ}$ . The eutectic temperature therefore lies between  $72.1^{\circ}$  and  $72.6^{\circ}$ . A 29 per cent. mixture was again made up, and melted. A thermometer was stirred round in the liquid to ensure complete mixing, and then lifted out, when a film of the mixture quickly solidified round the bulb. It was then enclosed in an air-bath, and gradually heated, until the mixture was noticed to flow down the thermometer and form a large drop on the end of the bulb. The temperature at which this occurred was accepted as the eutectic temperature.

Working with two different samples, the following results were obtained:

Experiment 1 .....	$72.4^{\circ}$	Experiment 2 .....	$72.3^{\circ}$
„ 1a .....	$72.3$	„ 2a .....	$72.4$

It was now necessary to obtain the initial freezing point of a mixture, the composition of which lies between 29 per cent. and that of the highest pair of analytical points on the second pair of curves. For this purpose a mixture containing 26 per cent. of the sodium salt was taken, that is, nearly the composition represented by the formula  $\text{NaPa}_3\text{HPa}$ . This experiment was also carried out by coating the thermometer bulb, but in this case the temperature accepted as the I.F.P. (or final melting point) was that at which

the drop on the end of the thermometer became quite transparent. The experiments gave the results:

Experiment 1 .....	71.8°
" 2 .....	71.7
" 3 .....	71.8

These results, when plotted in Fig. 4, are seen to agree very well with the analytical results, and practically to exclude the existence of a stable maximum in the second pair of curves before the second eutectic is reached.

The results given in table III., and plotted in Fig. 4, are liable to two sources of inaccuracy, namely, (1) analytical errors, and (2) divergence from the true composition of the solid phase by reason of adhering liquid.

The analytical error is insignificant for the purpose of the present work, the analyses being carried out in duplicate with reasonable agreement.

The second source of error is of greater importance, as one is entirely dependent on the results of analysis in fixing the composition of the solid phase. It might be argued that a solid phase of constant composition corresponding with each branch of the liquid phase curve really separates out, but that this is not recognised owing to incomplete separation from the mother liquor. This view can, however, be shown to be untenable by the following reasoning. Confining one's attention, in the first place, to the middle pair of curves (numbered II. on the diagram), let it be supposed that the true solid phase is one of constant composition, represented by some vertical line on the diagram. Then it must fulfil the condition that this vertical line cannot enter the space enclosed by the analytical curves, as, at the temperatures at which this occurred, a negative amount of wetting would have taken place. It can therefore only cut the solid and liquid phase curves at the point at which they touch each other. One can now assign a simple molecular composition to this constant solid phase, and calculate, or read off from the diagram, the amounts of liquid phase which would have to be associated with unit amount of this, in order to give the analytical results. If this composition corresponding with the second pair of curves be supposed to be that of the possible acid salt  $\text{NaPa}_3\text{HPa}$  (approximately 26 per cent. of sodium palmitate), the solid separated would have to be made up of about one part of the true solid phase and two parts of the liquid phase, a conclusion which is quite absurd. Any assumed composition lying to the right of this on the diagram would, of course, give even more unlikely results,

whilst no simple composition lying to the left exists which does not cut both curves in separate and well-substantiated points.

The same reasoning may be applied to the other pair of curves. Thus if the solid phase separating along the pair of curves numbered I. were the pure acid, this would have to be associated with about half its weight of liquid phase. The mixtures are here, however, not very viscous, and it is unlikely that such extensive wetting occurs. Along the pair of curves numbered III. the solid phase which suggests itself is the acid salt  $\text{NaPa,HPa}$ , which, however, contains more than 50 per cent. of the sodium salt, and would have to have been wetted with twice its weight of mother liquor to give the results obtained. In support of the above argument it may also be said that if a composition and temperature were so selected as to be represented by a point lying midway between the liquidus and solidus curves, a practically 50 per cent. mixture of solid and liquid was obtained, although no exact quantitative test of this could be carried out owing to loss on the glass of the apparatus.

The solid phase curve in the third branch undoubtedly suffers more from this wetting than in the other two branches, as the liquid phase is here much more viscous. Indeed, in order to effect a separation at all, matters had to be so arranged that there was much more liquid than solid present, otherwise the material would not flow down into the Gooch crucible. Two experiments are quoted (expts. 13 and 18) in table III. in which this precaution had not been taken. A little liquid phase was separated, and analysed, giving results which fell on the curve, but the solid, when removed from the apparatus, gave points which were well within the area enclosed by the liquidus and solidus curves.

It results from these experiments that no constant solid phases corresponding with acid salts in which the molar ratio  $\frac{\text{acid}}{\text{salt}} > 1$  separate out, whilst the separation of the acid salt  $\text{NaPa,HPa}$  is extremely doubtful, although this composition has not been covered by the experimental data.

The existence of the solid solutions which have been shown to occur is rendered very probable when we consider that the chemical "polarity" between palmitic acid and its sodium salt is relatively small owing to the extent of the carbon chain present in each case. This confers on both acid and salt such a predominating hydrocarbon character that the chemical polarity due to the different residual affinities of the  $\text{-CO}_2\text{H}$  and  $\text{-CO}_2\text{Na}$  groups is to a great extent obliterated. In confirmation of this view may be mentioned the fact that liquid mixtures of palmitic acid and

sodium palmitate show no trace of electrolytic dissociation, the liquid being practically a non-conductor of electricity.

The existence of solid solutions is of considerable interest and importance in relation to the nature of the phases which can separate from aqueous soap solutions, or which are present in the colloidal state in such solutions. It would appear probable that such phases may be simply solid solutions of acid and soap, or else phases, whether liquid or solid, of variable composition, containing the three components, fatty acid, sodium oxide, water.

It is intended to continue this investigation with the object of ascertaining the nature of the phases which can separate from the three-component system, fatty acid, sodium (or potassium) salt, solvent.

#### *Summary of Results.*

(1) The two-component system palmitic acid-sodium palmitate has been investigated over a range of compositions extending from the pure acid to a mixture containing about 38 per cent. of the salt, corresponding with the temperature range of 60° to 82°.

(2) The solid phases which separate under these conditions consist of three series of solid solutions.

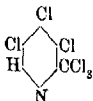
(3) No solid phases corresponding with definite compounds have been found to separate under the conditions of these experiments.

MUSPRATT LABORATORY OF PHYSICAL AND ELECTRO-CHEMISTRY,  
UNIVERSITY OF LIVERPOOL.

### CLXXXVIII.—*The Chlorine Derivatives of Pyridine.* *Part XI. Some Interactions of 3:4:5-Trichloropicolinic Acid and of its Derivatives.*

By WILLIAM JAMES SELL.

In former communications (Trans., 1905, **87**, 799; 1908, **93**, 1994) it was shown that one of the chief products of the chlorination of 2-methylpyridine is the compound having the constitution represented by the formula:



It was further pointed out that this compound undergoes decomposition when heated to 125–130° with 80 per cent. sulphuric

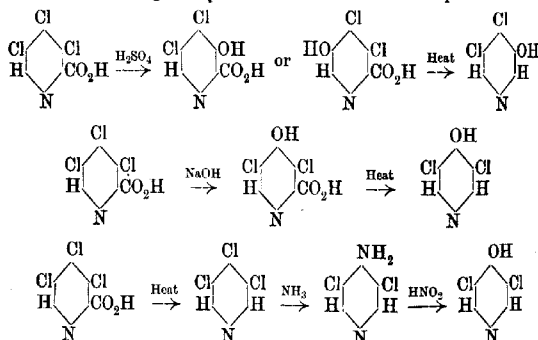


acid, giving mainly 3:4:5-trichloropicolinic acid, but that if the temperature was allowed to rise much above this point part of the acid is resolved into carbon dioxide and 3:4:5-trichloropyridine, which remains dissolved in the sulphuric acid.

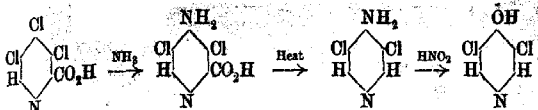
Examination of this decomposition of the hexachloropicoline on a larger scale revealed the fact that in addition to the above products a dichlorohydroxypicolinic acid was also formed in small quantity. This was separated from the later crops of 3:4:5-trichloropicolinic acid by crystallisation from water. The new compound separates from water in colourless, anhydrous needles, and is regarded as having the hydroxyl group in the position 3 or 5. It is resolved by heat without fusion or residue into carbon dioxide and the corresponding dichlorohydroxypyridine, which condenses in the cool part of the tube. An isomeric dichlorohydroxypicolinic acid is obtained from 3:4:5-trichloropicolinic acid by the action of alcoholic sodium hydroxide. The compound is regarded as 3:5-dichloro-4-hydroxypicolinic acid, and is also resolved by heat without fusion or residue into the corresponding dichlorohydroxypyridine\* and carbon dioxide.

Further, 3:4:5-trichloropicolinic acid reacts with ammonia when heated in a sealed tube, giving 3:5-dichloro-4-aminopicolinic acid, which on heating gives 3:5-dichloro-4-aminopyridine. The latter compound is converted by nitrosylsulphuric acid into 3:5-dichloro-hydroxy-4-pyridine, identical with that obtained by the action of alcoholic sodium hydroxide on 3:4:5-trichloropicolinic acid, and subsequent acidification and heating.

The above changes may for convenience be thus represented:



\* This nomenclature is employed for convenience only. The question as to whether this and similar substances are pyridone or hydroxypyridine derivatives is left quite open.



## EXPERIMENTAL.

*Formation of Dichloro-3(or 5)-hydroxypyridine from 3:4:5-Trichloropyridine-3-carboxylic Acid.*

This compound was separated from the mother liquors in the decomposition of hexachloropyridine by 80 per cent. sulphuric acid, and is doubtless formed from the chief product of this decomposition, namely, 3:4:5-trichloropyridine-3-carboxylic acid, by the displacement of a chlorine atom by an hydroxyl group. The substance separates from water in anhydrous, colourless, microscopic needles, which are moderately soluble in boiling water, sparingly so in cold water, and freely soluble in warm alcohol or ether:

0.124 gave 0.158  $\text{CO}_2$  and 0.0175  $\text{H}_2\text{O}$ .  $\text{C}=34.72$ ;  $\text{H}=1.56$ .

0.2055 „ 0.2868  $\text{AgCl}$ .  $\text{Cl}=34.50$ .

0.2053 „ 0.287  $\text{AgCl}$ .  $\text{Cl}=34.58$ .

$\text{C}_5\text{H}_3\text{O}_2\text{NCl}_2$  requires  $\text{C}=34.61$ ;  $\text{H}=1.44$ ;  $\text{Cl}=34.13$  per cent.

The compound decomposes without melting, being resolved into 4:5-dichloro-3-hydroxypyridine and carbon dioxide. An aqueous solution of the acid gives the following reactions: *Ferric chloride*: a deep brownish-red colour. *Cupric acetate*: bluish-grey, very sparingly soluble, crystalline precipitate. *Silver nitrate*: a gelatinous precipitate, very sparingly soluble in boiling water; the filtered hot liquid deposits needles of the silver salt on cooling.

The ammonium salt of the acid gave with barium chloride a copious precipitate consisting of fine needles.

Calcium chloride gave an immediate precipitate consisting of rosettes of needles, sparingly soluble in boiling water, from which it separates in tufts of silky needles.

*Formation of 4:5-Dichloro-3-hydroxypyridine from Dichloro-3(or 5)-hydroxypyridine-3-carboxylic Acid.*

When the preceding compound is heated in a wide glass tube in a gentle current of air it is resolved without melting or residue into carbon dioxide and 4:5-dichloro-3-hydroxypyridine, which forms a crystalline sublimate in the cool part of the tube. The sublimate is dissolved in boiling water, and on cooling crystallises in colourless, prismatic needles:

0.143 gave 0.2496 AgCl. Cl=43.16.  
 $C_8H_5ONCl_2$  requires Cl=43.27 per cent.

The aqueous solution gives no colour with ferric chloride. With silver nitrate a granular, crystalline precipitate slowly appears.

*Preparation of 3:5-Dichloro-4-hydroxypicolinic Acid from  
 3:4:5-Trichloropicolinic Acid or from Hexachloropicoline.*

When either 3:4:5-trichloropicolinic acid or hexachloropicoline is heated for some hours on the water-bath with excess of alcoholic sodium hydroxide in a flask with reflux, interaction takes place, as shown by the deposit of sodium chloride. The contents of the flask when diluted with water and acidified with hydrogen chloride deposit the acid in creamy-white, globular masses of minute needles, which after washing and recrystallisation from dilute alcohol still remained slightly coloured. The compound does not melt when heated, but is resolved without blackening or residue into carbon dioxide and 3:5-dichloro-4-hydroxypyridine. The substance is but moderately soluble in hot alcohol, acetone, or water, and sparingly so in these solvents in the cold:

0.3935 lost 0.058  $H_2O$  at  $144^\circ$ .  $H_2O=14.73$ .

0.158 gave 0.18662 AgCl. Cl=29.19.

$C_6H_3O_3NCl_2 \cdot 2H_2O$  requires  $H_2O=14.75$ ; Cl=29.09 per cent.

A warm saturated aqueous solution of the hydroxy-acid gives the following reactions: *Ferric chloride*: a deep red colour. *Cupric acetate*: a greyish-blue precipitate, consisting of groups of needles. *Silver nitrate*: rosettes of needles on keeping. The ammoniacal solution gave with: *Barium chloride*: a slight crystalline precipitate on keeping. *Calcium chloride*: a precipitate consisting of micaceous plates. *Silver nitrate*: gelatinous, white precipitate, sparingly soluble in boiling water.

*Formation of 3:5-Dichloro-4-hydroxypyridine from 3:5-Dichloro-4-hydroxypicolinic Acid.*

When 3:5-dichloro-4-hydroxypicolinic acid is gradually heated to about  $300^\circ$  it is resolved without previous fusion into carbon dioxide and 3:5-dichloro-4-hydroxypyridine, the latter condensing in crystals on the cool part of the apparatus. The decomposition may also be brought about by heating in glycerol, but loss of material is occasioned by the difficulty of separating the dichlorohydroxypyridine from the glycerol residue. On recrystallisation from dilute alcohol the substance separates in needles. It is readily soluble in alkalis, and separates on acidification in rosettes of needles:

0.150 gave 0.2606 AgCl. Cl=42.96.

$C_6H_9ONCl_2$  requires Cl=43.25 per cent.

An aqueous solution of the compound gives with: *Ferric chloride*: no change of colour. *Silver nitrate*: tufts of needles, slowly precipitated.

The ammoniacal solution gives with: *Barium chloride*: no precipitate, even after keeping. *Calcium chloride*: no precipitate at first, but after some time a crystalline deposit consisting of flat needles and plates.

*Conversion of 3:4:5-Trichloropicolinic Acid into 3:5-Dichloro-4-aminopicolinic Acid.*

Five tubes, each containing 2 grams of the acid and 30 c.c. of strong aqueous ammonia, were sealed and heated to  $140^\circ$  for several hours. The product was evaporated to remove the excess of ammonia, the amino-acid precipitated by hydrogen chloride, and after washing purified by crystallisation from water. The substance separates on slow cooling of the hot liquid in massive, prismatic, very faintly coloured crystals containing one molecule of water of crystallisation, and melting and decomposing at  $172^\circ$  (uncorr.):

0.3787 lost 0.0308  $H_2O$  at  $100^\circ$ .  $H_2O=8.13$ .

0.2450 gave 0.286  $CO_2$  and 0.06  $H_2O$ . C=31.83; H=2.71.

0.1713 „ 17.8 c.c.  $N_2$  at  $10^\circ$  and 762 mm. N=12.47.

0.242 (dried acid) gave 0.3345 AgCl. Cl=34.172.

$C_6H_4O_2N_2Cl_2 \cdot H_2O$  requires  $H_2O=8.0$ ; C=32; H=2.66;  
N=12.44 per cent.

$C_6H_4O_2N_2Cl_2$  requires Cl=34.29 per cent.

The aqueous solution gives with: *Ferric chloride*: a deep red colour. *Copper acetate*: a light blue, sparingly soluble precipitate consisting of rosettes of minute needles. *Ammoniacal silver nitrate*: a white, gelatinous precipitate, practically insoluble in boiling water. *Barium chloride and ammonia*: a slight, granular precipitate after some time.

*Conversion of 3:4:5-Trichloropyridine into 3:5-Dichloro-4-aminopyridine.*

Trichloropyridine (Trans., 1905, 87, 802) was heated in a sealed tube with a mixture of equal volumes of strong aqueous ammonia and alcohol for several hours at  $150^\circ$ . The contents of the tube after evaporation to dryness in a vacuum over sulphuric acid were washed with water to remove ammonium chloride, and the residue was crystallised from alcohol. The substance separates from alcohol in long needles, melting at  $161^\circ$  (uncorr.).

The same substance is also readily produced by heating the preceding compound (3:5-dichloro-4-aminopicolinic acid) a few degrees above its melting point, when it is resolved into carbon dioxide and 3:5-dichloro-4-aminopyridine. The substance crystallises from alcohol in long needles, melting at 161° (uncorr.):

0.216 gave 31.4 c.c. N<sub>2</sub> at 13° and 752 mm. N=16.99.

0.086 „ 0.1518 AgCl. Cl=43.64.

C<sub>5</sub>H<sub>4</sub>N<sub>2</sub>Cl<sub>2</sub> requires N=17.17; Cl=43.55 per cent.

*Conversion of 3:5-Dichloro-4-aminopyridine into 3:5-Dichloro-4-hydroxypyridine.*

A few grams of 3:5-dichloro-4-aminopyridine were dissolved in 80 per cent. sulphuric acid, mixed with an excess of nitrosylsulphuric acid, and heated on the water-bath until no further effervescence was visible. The liquid was poured into cold water, partly neutralised with sodium carbonate, and evaporated to a small bulk. On cooling, the substance separated in needles, and after solution in sodium carbonate and precipitation by dilute sulphuric acid, was crystallised from water, from which it separates in filamentous needles or in rosettes of needles. The qualitative reactions and general characters are identical with those of the substance produced above by other reactions. (Found: Cl=43.13. Calc., Cl=43.25 per cent.)

UNIVERSITY LABORATORY,  
CAMBRIDGE.

CLXXXIX.—*The Formation and Reactions of Imino-compounds. Part XVI. Reactions Leading to the Formation of Tricarballic Acid.*

By FERDINAND BERNARD THOLE and JOCELYN FIELD THORPE.

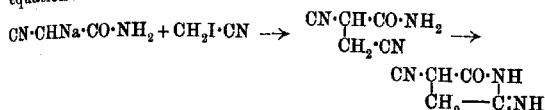
THE formation of imino-compounds by the internal coupling of an amino-group, present in an amide, with a nitrile group occupying the 3-position has already been demonstrated by the formation of a series of condensation products from ketones and cyanoacetamide (this vol., p. 422).

Thus it was found that when acetone is condensed with cyanoacetamide in the presence of piperidine the imino-compound is formed:

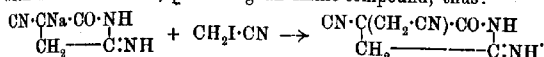


It was therefore to be expected that cyanoamides having the cyano-group in the  $\gamma$ -position would pass into an imino-derivative of the five-membered ring with even greater ease. The present communication deals with two reactions of this type.

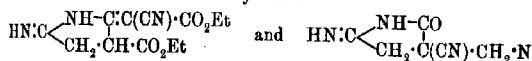
In the first place, it was hoped to prepare a simple compound of this series by the interaction of the sodium compound of cyanoacetamide with iodoacetonitrile in accordance with the equation:



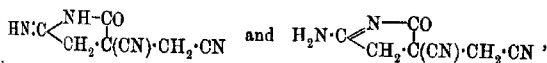
Experiment showed, however, that it was not possible to isolate the condensation product of this formula, because, at the moment of its formation, interaction with unchanged sodiocyanoacetamide ensued, yielding a sodium compound, which then reacted further with iodoacetonitrile, producing an imino-compound, thus:



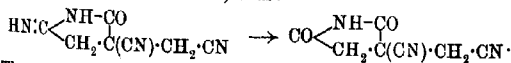
This substance is in many respects analogous to the compound prepared by Best and Thorpe (Trans., 1909, **95**, 1506) by the interaction of the sodium derivative of ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate and iodoacetonitrile, a relationship which is clearly seen when the two formulae are written side by side:



In the previous case the compound was shown to react in its tautomeric imino-amino-forms, but to have only a short imino-phase. In the present instance there is no doubt that the imino-compound also reacts in the two forms:



because it not only readily dissolves in dilute hydrochloric acid and is precipitated for the most part unchanged on the addition of sodium acetate, but when the acid solution is warmed, complete hydrolysis to the imide ensues, thus:



The stability of the six-membered ring towards alkali, which was commented on in the previous communication, is also shown by the compound under discussion, for, when it is boiled with alkali hydroxides, it is transformed into the imide of the dicarboxylic

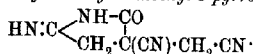


$\text{CN}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CN}$ , in this respect had yielded negative results, but the conclusions were not regarded as definite, owing to the very soluble character of the products formed from this nitrile. In the present instance the formation of any imino-compound by the action of sodium ethoxide could have been at once detected, but no such formation occurred.

It is interesting to note that the above nitrile ester can be readily hydrolysed to tricyanohydrin,  $\text{CN}\cdot\text{CH}_2\cdot\text{CH}(\text{CN})\cdot\text{CH}_2\cdot\text{CN}$ , a substance which, although it has played an important part in the synthesis of tricarballic acid from glycerol, does not appear to have been isolated. It is a well defined, crystalline substance, melting at  $47^\circ$ .

#### EXPERIMENTAL.

##### *2-Imino-4-cyano-4-cyanomethyl-5-pyrrolidone,*



This substance is prepared by dissolving 4.6 grams of sodium in 60 c.c. of alcohol, adding 16.8 grams of cyanoacetamide, and then 33 grams of iodoacetoneitrile in small portions at a time. The reaction is vigorous, and must be checked by cooling; when finished, the imino-compound separates in the crystalline form when the side of the containing vessel is scratched. It is best purified by dissolving in cold dilute hydrochloric acid, and re-precipitating by the addition of aqueous sodium acetate, but can be obtained crystalline from warm water in small, colourless prisms, which carbonise, without melting, at  $215\text{--}220^\circ$ :

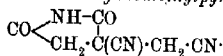
0.1715 gave 0.3255  $\text{CO}_2$  and 0.0562  $\text{H}_2\text{O}$ .  $\text{C}=51.81$ ;  $\text{H}=3.62$ .

0.1058 „ 31.8 c.c.  $\text{N}_2$  at  $19^\circ$  and 739 mm.  $\text{N}=34.4$ .

$\text{C}_7\text{H}_6\text{ON}_4$  requires  $\text{C}=51.8$ ;  $\text{H}=3.7$ ;  $\text{N}=34.6$  per cent.

The imino-compound is soluble in dilute mineral acids, and also dissolves in cold aqueous alkaline hydroxides. It is insoluble in cold solutions of alkali carbonates, and when boiled with water is slowly hydrolysed with evolution of ammonia.

##### *4-Cyano-2:5-diketo-4-cyanomethylpyrrolidine,*



The formation of this substance from the imino-compound may be effected by dissolving the base in dilute hydrochloric acid, and then raising the solution to the boiling point. The imide usually separates completely when the solution is cooled, but if this is not the case it must be isolated by extracting the solution with ether.



It can be purified by crystallisation from water, and obtained in small, colourless prisms, which melt at  $137-138^{\circ}$ , and blacken at a high temperature:

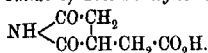
0.2006 gave 0.3770  $\text{CO}_2$  and 0.0576  $\text{H}_2\text{O}$ .  $\text{C}=51.31$ ;  $\text{H}=3.20$ .

0.1430 „ 31.7 c.c.  $\text{N}_2$  at  $18^{\circ}$  and 750 mm.  $\text{N}=25.8$ .

$\text{C}_7\text{H}_5\text{O}_2\text{N}_3$  requires  $\text{C}=51.5$ ;  $\text{H}=3.1$ ;  $\text{N}=25.8$  per cent.

The imide dissolves in aqueous alkali carbonates, and yields a faintly acid solution with water.

*The Imide of Tricarballic Acid,*



Five grams of the imino-compound are boiled with excess of potassium hydroxide solution until free from ammonia, when the solution is acidified and extracted with ether. The syrup which remains on evaporating the ether is heated at  $180^{\circ}$  until all carbon dioxide has been evolved, and the residue is then rubbed with dry ether. The solid obtained in this manner crystallises from benzene in small prisms, melting at  $127-128^{\circ}$ :

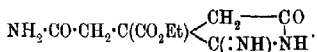
0.1688 gave 0.2844  $\text{CO}_2$  and 0.0673  $\text{H}_2\text{O}$ .  $\text{C}=45.94$ ;  $\text{H}=4.46$ .

$\text{C}_6\text{H}_7\text{O}_4\text{N}$  requires  $\text{C}=45.9$ ;  $\text{H}=4.4$  per cent.

The imide is readily soluble in water or alcohol, but sparingly so in ether or benzene.

When any one of the above compounds is boiled with dilute sulphuric acid, tricarballic acid, melting at  $165^{\circ}$ , is formed. (Found,  $\text{C}=41.10$ ;  $\text{H}=4.5$ .  $\text{C}_6\text{H}_5\text{O}_6$  requires  $\text{C}=40.9$ ;  $\text{H}=4.5$  per cent.) The acid can be obtained from the product of hydrolysis by extraction with ether.

*Ethyl 2-Imino-3-carbamylmethyl-5-pyrrolidone-3-carboxylate,*



To a solution of 5.8 grams of sodium in 70 c.c. of alcohol, 29 grams of ethyl cyanoacetate are added, and then 23.5 grams of chloroacetamide, the reaction being carried to completion by boiling on the water-bath for one hour. When the solution is evaporated free from most of the alcohol, water precipitates the solid imino-compound, which crystallises from water in voluminous, matted needles, melting at  $191^{\circ}$  with evolution of gas:

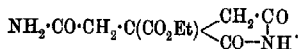
0.1613 gave 0.2806  $\text{CO}_2$  and 0.0817  $\text{H}_2\text{O}$ .  $\text{C}=47.41$ ;  $\text{H}=5.62$ .

0.1331 „ 20.9 c.c.  $\text{N}_2$  at  $18^{\circ}$  and 745 mm.  $\text{N}=18.2$ .

$\text{C}_9\text{H}_{13}\text{O}_7\text{N}_3$  requires  $\text{C}=47.6$ ;  $\text{H}=5.7$ ;  $\text{N}=18.5$  per cent.

The imino-compound is readily soluble in dilute hydrochloric acid, and is precipitated, for the most part unchanged, when sodium acetate is added to the solution. It can be recrystallised from alcohol.

*Ethyl 2:5-Diketo-3-carbamylmethylpyrrolidine-3-carboxylate,*



The transformation of the imino-compound into this imide can be effected by heating a concentrated solution of it in dilute hydrochloric acid to the boiling point, and allowing the imide to crystallise on cooling. It forms small needles, which melt at 127°:

0.1921 gave 0.3327 CO<sub>2</sub> and 0.0935 H<sub>2</sub>O. H=47.23; H=5.41.

C<sub>9</sub>H<sub>12</sub>O<sub>5</sub>N<sub>2</sub> requires C=47.4; H=5.3 per cent.

The imide is readily soluble in warm water.

Both the above compounds yield tricarballic acid on complete hydrolysis with dilute sulphuric acid.

*Ethyl αβ'-Tricyanoisobutyrate, CN·CH<sub>2</sub>·C(CN)(CO<sub>2</sub>Et)·CH<sub>2</sub>·CN.*

This substance is formed in practically quantitative yield when 4.6 grams of sodium dissolved in 22.6 grams of alcohol are mixed with 22.6 grams of ethyl cyanoacetate, and then with 33.4 grams of iodoacetoneitrile. The reaction is finished after heating on the water-bath for half an hour. The ester, which is extracted by ether in the usual manner, boils at 205°/18 mm.:

0.1970 gave 0.4089 CO<sub>2</sub> and 0.0813 H<sub>2</sub>O. C=56.61; H=4.58.

C<sub>9</sub>H<sub>9</sub>O<sub>2</sub>N<sub>3</sub> requires C=56.5; H=4.7 per cent.

*αβγ-Tricyanopropane (Tricyanohydrin),*  
CN·CH<sub>2</sub>·CH(CN)·CH<sub>2</sub>·CN.

Ten grams of ethyl αβ'-tricyanoisobutyrate are mixed with an equal volume of water, and the same volume of a 50 per cent. solution of potassium hydroxide. The oil dissolves when the mixture is shaken, and the solution is then at once rendered acid by acetic acid and raised to the boiling point. Carbon dioxide is eliminated, and an oil separates which solidifies on cooling. The compound is best recrystallised from ether, when it separates in long, colourless needles, melting at 47°:

0.1786 gave 0.3987 CO<sub>2</sub> and 0.0701 H<sub>2</sub>O. C=60.88; H=4.36.

C<sub>6</sub>H<sub>3</sub>N<sub>3</sub> requires C=60.5; H=4.2 per cent.

The nitrile is soluble in hot water, and separates as an oil on cooling. It is sparingly soluble in cold ethyl alcohol or ether. When boiled with dilute sulphuric acid it is hydrolysed to tricarballic acid.

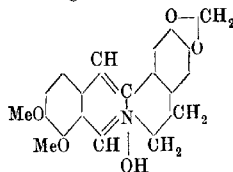
We were unable to detect the formation of any imino-compound from this nitrile by treatment with sodium ethoxide.

THE SORBY RESEARCH LABORATORY,  
THE UNIVERSITY, SHEFFIELD.

### CXC.—isoQuinoline Derivatives. Part VI. neoOxyberberine.

By FRANK LEE PYMAN.

THE main features of the constitution of berberine were determined by Perkin (Trans., 1889, 55, 63; 1890, 57, 992) by a study of its oxidation products. Later, Gadamer (*Arch. Pharm.*, 1905, 243, 42) and Perkin and Robinson (Trans., 1910, 97, 321) proposed certain alterations in Perkin's original formula, and the constitution of this alkaloid is now recognised as that given below:

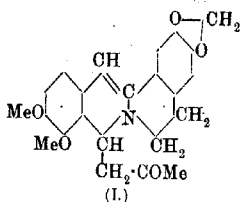


Berberine.

Perkin found that the careful oxidation of berberine, even in small quantities and with a limited amount of permanganate (in the presence of potassium carbonate), led to the formation of a mixture of a large number of products. This fact is readily explained by the above formula, by which the molecule is shown to contain two double linkings, at either or both of which oxidation would be expected to take place.

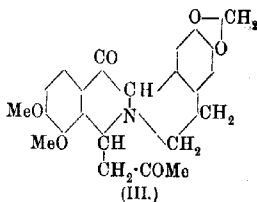
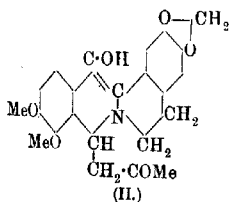
Now it seemed of interest to study the oxidation of a derivative of berberine in which one of these points of attack was protected, for in that case a more uniform oxidation product or a less complicated mixture of products should result. With this object in view the oxidation of berberineacetone was undertaken. This compound was first described by Gaze (*Zeit. Naturwiss. Halle*, 1890, 62, 399)

as a molecular compound before the nature of berberine was fully understood, but Gadamer (*loc. cit.*) recognised it later as a condensation product of the same type as anhydrocotarnineacetone, and suggested for it the formula (I), which satisfactorily explains its properties:



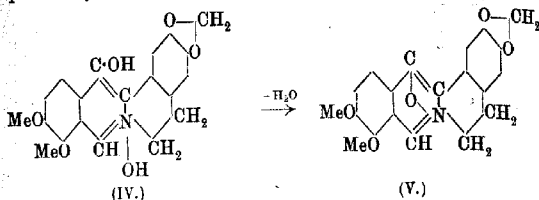
Reference to the formula will show that this compound only contains one double linking. By hydrolysing it with dilute acids, however, the acetone can be removed and the second double linking replaced with the formation of berberine hydrochloride; this reaction is common to all similarly constituted isoquinoline derivatives, such as anhydrocotarnineacetone.

On oxidising berberineacetone,  $C_{23}H_{23}O_5N$ , in acetone solution with aqueous permanganate, a new colourless compound,  $C_{23}H_{23}O_6N$ , containing one more atom of oxygen, resulted. This substance, which was isolated in a yield of about 45 per cent. of the theoretical, has been designated *neoxyberberineacetone*. Oxidation of berberineacetone would naturally be expected to take place at the double linking, and *neoxyberberineacetone* would then have the formula (II) or the tautomeric form (III). The first of these, however, is eliminated by the insolubility of the compound in aqueous sodium hydroxide, but formula (III) satisfactorily accounts for its behaviour and that of its derivatives:

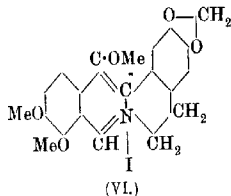


On hydrolysing *neoxyberberineacetone* with dilute mineral acids, acetone is split off, and the salt of a quaternary base is produced, as is the case with all similarly constituted acetone-condensation products. The base obtained on treating this salt with alkali, however, is not the corresponding quaternary base,  $C_{20}H_{19}O_6N$  (IV).

but a substance,  $C_{20}H_{17}O_5N$ , derived from it by the elimination of the elements of water. This compound is isomeric with oxyberberine and the isooxyberberine recently described by Bland, Perkin, and Robinson (Proc., 1911, 27, 59), and has been designated *neooxyberberine* (V). Its formation from the enolic form of the quaternary base may be represented as follows:



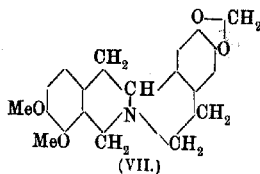
This formula depicts *neooxyberberine* as a phenolbetaine, and this is justified by its behaviour, for it has the usual characteristics of such compounds (compare Decker and Dunant, *Annalen*, 1908, 358, 296). Thus, it is golden-brown in colour, crystallises with a molecule of either alcohol or chloroform of crystallisation, and is liberated from its salts by means of sodium carbonate. Its salts with acids are of a much less intense colour than the base, and are derived from formula IV or the corresponding ketonic form by substitution. Definite proof of its phenolbetaine nature, however, is afforded by the fact that it yields with methyl iodide the iodide of a quaternary base containing three methoxyl groups, that is, one more than the parent compound. This substance, *methoxyberberinium iodide*, has the formula (VI) given below, and its



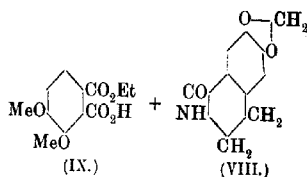
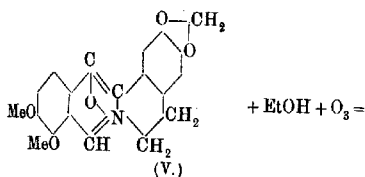
quaternary nature is shown by the fact that the corresponding base is not liberated by means of sodium carbonate, sodium hydroxide being requisite for this purpose.

*neooxyberberine* also shows the behaviour, associated with phenolbetaines, of forming salts containing two molecules of the base to one of acid (compare Trans., 1910, 97, 269); thus the hydrochloride has the formula  $HO\cdot R:N\cdot O\cdot R:NCl$ , although the hydriodide has the normal constitution  $HO\cdot R:N\cdot I$ .

*neo*Oxyberberine readily furnishes tetrahydroberberine (VII) in good yield when reduced by means of tin and hydrochloric acid:



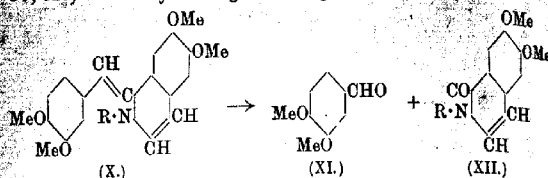
The most remarkable property of this compound, however, is the facility with which it undergoes spontaneous oxidation when exposed to the air in chloroform solution. So large a quantity as 25 grams of *neo*oxyberberine (containing 1EtOH) appeared to be completely decomposed after exposure to the air for eighteen days, and the reaction product gave 1-keto-6:7-methylenedioxytetrahydroisoquinoline (VIII) in a yield amounting to 53 per cent. of the theoretical, together with a quantity of one of the ethyl hydrogen hemipinates, probably the 1-ester (IX). Small quantities of other crystalline products, and a considerable amount of amorphous material, were produced at the same time. The formation of the two compounds isolated may be represented as follows:



1-Keto-6:7-methylenedioxytetrahydroisoquinoline was, of course, one of the oxidation products of berberine isolated by Perkin (*loc. cit.*).

The degradation of *neo*oxyberberine in this manner recalls the analogous cleavage of the somewhat similarly constituted *N*-alkylisopapaverines (X) into veratraldehyde (XI) and dimethoxy-

*N*-alkylisoquinolones (XII), which Decker and Klausner (*Ber.*, 1904, 37, 520) effected by drawing air through dilute alkaline solutions:



#### EXPERIMENTAL.

The berberineacetone used in this investigation was prepared from commercial berberine sulphate by the method described by Gaze (*loc. cit.*). It melted and decomposed at 175° (corr.). (Found, C=70.0; H=5.9. Calc., C=70.2; H=5.9 per cent.)

#### *Oxidation of Berberineacetone. Formation of neoOxyberberineacetone.*

The oxidation of berberineacetone,  $C_{23}H_{25}O_2N$ , to neoOxyberberineacetone,  $C_{23}H_{25}O_6N$ , involves the addition of one atom of oxygen. It has, however, been found advantageous to employ a quantity of permanganate corresponding with two atoms for the oxidation, and the following conditions have been found to give a satisfactory result.

Five and a-half grams of potassium permanganate were dissolved in 500 c.c. of water, and the solution was poured into a solution of 10 grams of berberineacetone in 500 c.c. of acetone at the laboratory temperature. The mixture was kept for fifteen minutes, then filtered from the separated manganese hydroxide, and the liquor somewhat evaporated on the water-bath. During the removal of the acetone, a quantity of crystals mixed with some resinous matter separated, and after nearly all the acetone had evaporated, the solid was collected, and ground with a little ethyl acetate, when 4.0 to 4.9 grams of neoOxyberberineacetone, melting at 228–229° (corr.), were obtained. This product has a more or less marked buff colour, but is otherwise pure. It may be decolorised by crystallisation from alcohol, using animal charcoal.

neoOxyberberineacetone,  $C_{23}H_{25}O_6N$  (III, p. 1691).

This base crystallises from absolute alcohol in colourless, transparent, hexagonal and trigonal plates, which melt and decompose at 228–229° (corr.), forming a dark red liquid. It is insoluble in water, and sparingly or very sparingly soluble in the usual organic

solvents, with the exception of warm chloroform, in which it is moderately easily soluble:

0.1527 gave 0.3173  $\text{CO}_2$  and 0.0786  $\text{H}_2\text{O}$ .  $\text{C}=67.4$ ;  $\text{H}=5.8$ .

0.1900 „ 5.8 c.c.  $\text{N}_2$  at  $24^\circ$  and 770 mm.  $\text{N}=3.6$ .

$\text{C}_{23}\text{H}_{23}\text{O}_5\text{N}$  requires  $\text{C}=67.5$ ;  $\text{H}=5.7$ ;  $\text{N}=3.4$  per cent.

This base dissolves to some extent in cold dilute hydrochloric acid, but soon crystallises out as a very sparingly soluble, colourless hydrochloride. When warmed with dilute hydrochloric acid, the base yields a yellow solution, and eventually yellow, silky needles consisting of *neooxyberberine* semihydrochloride. *neooxyberberine*-acetone is not attacked by hot aqueous sodium hydroxide, in which it is insoluble.

*neooxyberberine*,  $\text{C}_{20}\text{H}_{17}\text{O}_5\text{N}$  (V, p. 1692).

Twelve grams of *neooxyberberine*-acetone were boiled for two hours under a reflux condenser with 1.2 litres of 1 per cent. aqueous hydrochloric acid. The almost insoluble powder gradually dissolved, forming a deep canary-yellow solution, from which a large quantity of curved, silky, yellow needles separated while the boiling was still in progress. The needles, which decomposed at  $227^\circ$  (corr.), consisted of *neooxyberberine* semihydrochloride; they were not, however, collected, but converted into the base by adding 200 c.c. of 10 per cent. aqueous sodium hydroxide to the liquor and boiling it for another twenty minutes. The almost insoluble *neooxyberberine* was then collected, and crystallised from alcohol, when 9.6 grams of the pure base (containing 1 EtOH) were obtained; this yield amounts to 84 per cent. of the theoretical.

*neooxyberberine* crystallises from alcohol in long, golden-brown, prismatic needles, which contain one molecule of alcohol of crystallisation. It melts and decomposes at  $275^\circ$  (corr.), and is almost insoluble in boiling water, sparingly soluble in cold alcohol and most of the other usual organic solvents, but easily soluble in chloroform or hot alcohol:

0.1562 \* lost 0.0176 at  $100^\circ$ .  $\text{C}_2\text{H}_6\text{O}=11.3$ .

0.1528 \* gave 0.3702  $\text{CO}_2$  and 0.0800  $\text{H}_2\text{O}$ .  $\text{C}=66.1$ ;  $\text{H}=5.9$ .

$\text{C}_{20}\text{H}_{17}\text{O}_5\text{N} \cdot \text{C}_2\text{H}_6\text{O}$  requires  $\text{C}=66.5$ ;  $\text{H}=5.8$ ;  $\text{C}_2\text{H}_6\text{O}=11.6$  per cent.

0.1386 † gave 0.3469  $\text{CO}_2$  and 0.0615  $\text{H}_2\text{O}$ .  $\text{C}=68.3$ ;  $\text{H}=5.0$ .

0.1454 † „ 5.0 c.c.  $\text{N}_2$  at  $20^\circ$  and 773 mm.  $\text{N}=4.1$ .

0.2102 † „ , by Zeisel's method, 0.2758 AgI.  $\text{MeO}=17.3$ .

$\text{C}_{20}\text{H}_{17}\text{O}_5\text{N}$  requires  $\text{C}=68.3$ ;  $\text{H}=4.9$ ;  $\text{N}=4.0$ ;

$2\text{MeO}=17.7$  per cent.

\* Air-dried.

† Dried at  $100^\circ$ .



The molecular weight was determined by the ebullioscopic method in glacial acetic acid:

0.2344 † in 16.75 gave  $\Delta t$  0.11°. M.W. = 322.

0.4988 † „ 16.75 „  $\Delta t$  0.20°. M.W. = 377.

$C_{20}H_{17}O_5N$  requires M.W. = 351.

*neo*Oxyberberine yields with acids sparingly soluble salts; it is insoluble in aqueous sodium hydroxide.

The *semihydrochloride* crystallises from water or alcohol in long, deep yellow, curved, silky needles, which decompose at 227° (corr.). It is very sparingly soluble in boiling water, and sparingly so in boiling alcohol. After crystallisation from water, and drying in the air, this salt has the composition  $(C_{20}H_{17}O_5N)_2 \cdot HCl \cdot 3H_2O$ :

0.1378 \* gave 0.3058  $CO_2$  and 0.0676  $H_2O$ . C = 60.5; H = 5.5.

0.1566 \* „ 0.0294 AgCl. Cl = 4.6.

0.1266 \* lost 0.0090 at 110°.  $H_2O$  = 7.1.

$(C_{20}H_{17}O_5N)_2 \cdot HCl \cdot 3H_2O$  requires C = 60.5; H = 5.2; Cl = 4.5;

$H_2O$  = 6.8 per cent.

The *hydriodide* crystallises from water in deep yellow needles, which decompose at 275° (corr.). It is very sparingly soluble in water, and crystallises with  $1H_2O$ :

0.2555 \* lost 0.0099 at 100°.  $H_2O$  = 4.0.

$C_{20}H_{17}O_5N \cdot HI \cdot H_2O$  requires  $H_2O$  = 3.7 per cent.

0.2456 † gave 0.4532  $CO_2$  and 0.0834  $H_2O$ . C = 50.3; H = 3.8.

0.3630 † „ 0.1780 AgI. I = 26.5.

$C_{20}H_{17}O_5N \cdot HI$  requires C = 50.1; H = 3.8; I = 26.5 per cent.

#### *Methoxyberberinium Salts* (VI, p. 1692).

*Methoxyberberinium iodide* was prepared in almost theoretical yield by heating *neo*oxyberberine with methyl iodide in a sealed tube at 100° for two hours. It crystallises from boiling water, in which it is somewhat sparingly soluble, in golden-brown, prismatic plates, which melt to a black liquid at 256° (corr.), after sintering a few degrees earlier. It is anhydrous:

0.1651 gave 0.3086  $CO_2$  and 0.0634  $H_2O$ . C = 51.0; H = 4.3.

0.1510 „ 0.0722 AgI. I = 25.8.

0.2158 „ „ by Zeisel's method, 0.2989 AgI. MeO = 18.3.

$C_{21}H_{20}O_5NI$  requires C = 51.1; H = 4.1; I = 25.7;

3MeO = 18.9 per cent.

*Methoxyberberinium chloride* was prepared from the iodide by double decomposition with silver chloride. It is very readily soluble in water, and crystallises from this solvent in long, yellow needles, which contain 3 molecules of water of crystallisation, and

† Dried at 100°.

\* Air-dried.

melt at about  $117^{\circ}$  (corr.). It suffers decomposition when heated at  $100^{\circ}$ :

0.4000 \* lost 0.0470 in a vacuum over  $\text{H}_2\text{SO}_4$ .  $\text{H}_2\text{O}=11.7$ .

0.1982 \* gave, by Zeisel's method, 0.2971 AgI.  $\text{MeO}=19.8$ .

$\text{C}_{21}\text{H}_{20}\text{O}_5\text{NCl}\cdot 3\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}=11.9$ ;  $3\text{MeO}=20.4$  per cent.

After being dried in a vacuum over sulphuric acid:

0.1331 gave 0.3040  $\text{CO}_2$  and 0.0619  $\text{H}_2\text{O}$ .  $\text{C}=62.3$ ;  $\text{H}=5.2$ .

$\text{C}_{21}\text{H}_{20}\text{O}_5\text{NCl}$  requires  $\text{C}=62.7$ ;  $\text{H}=5.0$  per cent.

Aqueous solutions of this salt remain clear on the addition of sodium carbonate, but give with sodium hydroxide a yellow, amorphous precipitate, which is readily extracted by ether.

#### *Reduction of neoOxyberberine. Formation of Tetrahydroberberine.*

Ten grams of neoxyberberine were reduced by boiling with granulated tin and a large excess of hydrochloric acid in alcoholic solution until the originally yellow liquid had become nearly colourless. The liquor was then decanted from the tin, sufficiently evaporated to remove most of the alcohol, and diluted with about twice its volume of water, when a tin double salt separated, which was at first amorphous, but quickly became crystalline. This was collected, dissolved in about a litre of boiling water, treated with hydrogen sulphide, filtered from tin sulphide, and precipitated with aqueous sodium carbonate, when an oil separated which became partly crystalline on scratching. When this product was boiled with a little alcohol, 6.0 grams of tetrahydroberberine remained as a nearly colourless, chalky solid, which melted at  $168-169^{\circ}$  (corr.). The melting point of the base was unchanged by crystallising it from alcohol, and suffered no depression when the base was mixed with tetrahydroberberine prepared by the reduction of berberine. The identity of the base was further established by analysis (Found,  $\text{C}=70.7$ ;  $\text{H}=6.3$ . Calc.,  $\text{C}=70.8$ ;  $\text{H}=6.2$  per cent.), and also by the analysis of its hydrochloride, which crystallised from water in lozenge-shaped plates, melting and decomposing at  $248-250^{\circ}$  (corr.). (Found,  $\text{C}=63.6$ ;  $\text{H}=6.0$ ;  $\text{Cl}=9.4$ . Calc.,  $\text{C}=63.9$ ;  $\text{H}=5.9$ ;  $\text{Cl}=9.4$  per cent.)

#### *Spontaneous Oxidation of neoOxyberberine.*

Twenty-five grams of neoxyberberine (containing 1EtOH) were dissolved in 300 c.c. of chloroform, and kept for five weeks in a nearly full closed bottle in the dark. A considerable quantity of orange, yellowish-brown plates gradually crystallised out, and proved to be neoxyberberine containing a molecule of chloroform of crystal-

\* Air-dried.

lisation. After being dried in the air overnight, the crystals were found to have slightly effluoresced, and on warming them chloroform was readily given off:

0.2015 \* lost 0.0487 at 100°. Loss = 24.2.

$C_{20}H_{17}O_2N \cdot CHCl_3$  requires  $CHCl_3 = 25.4$  per cent.

The crystals decomposed at 275° (corr.) when heated either alone or mixed with the base containing alcohol of crystallisation. The chloroform mother liquor left on evaporation a crystalline mass of *neo*oxyberberine in an almost pure condition (m. p. 260°). *neo*Oxyberberine is therefore not attacked by chloroform in the absence of air.

Twenty-five grams of *neo*oxyberberine (containing 1EtOH) were then dissolved in 300 c.c. of chloroform, and exposed to the air in a wide-mouthed glass bottle in a dark cupboard. After keeping for two days a drop of the solution readily gave a crystalline residue, but after five days only an amorphous residue was obtained in this way. The solution was exposed to the air for eighteen days in all, the chloroform lost on evaporation being replaced from time to time, and the original intense yellowish-brown colour gave place to a brown port-wine shade. The liquid was then filtered from a trace of yellow insoluble matter, extracted several times with dilute aqueous sodium carbonate to remove the acidic constituents, and the extract (*E*) set aside. The chloroform solution was then dried with anhydrous potassium carbonate, and evaporated nearly to dryness, when the residue became partly crystalline. It was mixed with a little benzene, filtered, and the residual pink, chalky, crystalline mass washed with benzene. From the filtrate only very small quantities of crystalline compounds were isolated, the chief constituent being a reddish-brown, amorphous substance. The air-dried, crystalline mass amounted to 8.3 grams, and melted at about 155°; on recrystallisation from benzene it gave first 4.8 grams of 1-keto-6:7-methylenedioxytetrahydroisoquinoline, melting at 185—186° (corr.). Perkin (*loc. cit.*) gives 181—182°. (Found, C=62.4; H=4.9. Calc., C=62.8; H=4.8 per cent.)

The benzené mother liquors gave on evaporation several small crops of crystals, melting at about 140°. On recrystallising these from water, however, a further 1.6 grams of 1-keto-6:7-methylenedioxytetrahydroisoquinoline separated, making in all 6.4 grams, that is, 53 per cent. of the theoretical; the aqueous mother liquors contained hemipinic acid.

The sodium carbonate extract (*E*) was acidified with hydrochloric acid, and completely extracted with ether. The ethereal extract was dried, and evaporated to low bulk, when 2.9 grams of 1-ethyl

\* Air-dried.

hydrogen hemipinate separated in large, clear, colourless prisms, which melted at  $148-149^{\circ}$  (corr.), after drying at  $100^{\circ}$ . The ethereal filtrate on evaporation to dryness gave 3.1 grams of a slightly sticky, pink, crystalline mass, and on recrystallising this from water, using animal charcoal, a further 1.3 grams of 1-ethyl hydrogen hemipinate were obtained in long, colourless needles, which contained  $1\text{H}_2\text{O}$ , and melted at  $148-149^{\circ}$  (corr.), after drying at  $100^{\circ}$ . (Found, C=56.5; H=5.6. Calc., C=56.7; H=5.6 per cent.)

On saponifying this acid with 10 per cent. aqueous sodium hydroxide, acidifying, and extracting with ether, pure hemipinic acid was obtained. This melted and effervesced at  $184-185^{\circ}$  (corr.), solidified again on cooling, and then melted at about  $165^{\circ}$ . (Found, C=52.9; H=4.8. Calc., C=53.1; H=4.5 per cent.)

The ethyl hydrogen hemipinate thus obtained gave no coloration with ferric chloride in aqueous solution. It is therefore described as the 1-ester, since Wegscheider (*Monatsh.*, 1895, 16, 38) states that the 1- and 2-ethyl hydrogen hemipinates are distinguished by the fact that the 2-ester gives with ferric chloride in aqueous solution a yellow coloration and turbidity, whilst the 1-ester does not. The ethyl hydrogen hemipinate from neooxyberberine also agrees better in melting point with the 1-ester (m. p.  $146.5-148.3^{\circ}$ ) than with the 2-ester (m. p.  $144.5-145^{\circ}$ ). Wegscheider's 1-ester, however, contained no water of crystallisation, whilst the 2-ester crystallised from water in long needles containing  $1\text{H}_2\text{O}$ .

THE WELLCOME CHEMICAL WORKS.  
DARTFORD, KENT.

# CCXI. — *The Absorption Spectra of Various Chlorine and Bromine Derivatives of Benzene and Toluene as Vapours, in Solution and in Thin Films.*

By JOHN EDWARD PURVIS.

The author has already given an account of the absorption spectra of monochloro- and monobromo-benzene as vapours, in solution, and in thin films (this vol., p. 811). The chief results proved that the vapours of these two substances exhibited a considerable number of bands which could be arranged in various groups; that equimolecular solutions in alcohol exhibited seven wide diffuse bands; and that very thin films exhibited seven wide diffuse bands which were also comparable with the solution bands.

The investigation has been continued with *o*- and *m*-dichloro- and

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dibromo-benzene, and with *o*- and *m*-chloro- and bromo-toluene. The apparatus employed has been described in previous communications (*loc. cit.*).

## Vapours.—*o*-Dichlorobenzene.

TABLE I.

The absorption bands in the vapour of *o*-dichlorobenzene at various temperatures and pressures in a column 200 mm. long and 20 mm. diameter.

Abbreviations: v.w.=very weak; w.=weak; m.w.=moderately weak; str.=strong; m.str.=moderately strong; narr.=narrow.

	19°.	30°.	45°.	60°.
	763 mm.	807 mm.	833 mm.	863 mm.
	λ.	λ.	λ.	λ.
A.	2780 v.w.	2780 v.w.	2770 v.w. 2768 str. 2765 m.w.	No bands.  The rays were absorbed from about λ 2840, the Cd. lines 2748 and 2578 being visible.
	2779 v.w.	2779 v.w.		
	2776 m.w.	2777 v.w.		
	2774 m.w.	2775 w.		
	2773 m.w.	2773 w.		
	2770 w., narr.	2770 m.w.		
	2768 str.	2768 str.		
	2766 m.w.	2765 m.str.		
	2765 m.w.	2764 m.str.		
	2762 m.str.	2762 m.str.		
B.	2760 str.	2760 str.	2759 m.w. 2757 w., narr. 2754 w., narr. 2752 w., narr. 2750 w., narr.	75°. 893 mm. λ.  No bands.  The rays were absorbed from about λ 2850.
	2757 w., narr.	2757 w., narr.		
	2754 w., narr.	2754 w., narr.		
	2751 w., narr.	2751 w., narr.		
	2745 v.w.	2746 v.w.		
	2740 v.w.	2741 v.w.		
	2738 v.w.	2738 v.w.		
	2737 v.w.	2737 v.w.		
	2706 v.w.	2703 v.w. 2696 v.w. 2690 v.w. 2689 v.w. 2686 v.w. 2683 m.w. 2617 v.w. 2614 v.w. 2606 w. 2595 v.w.		
	2702 m.str.			
2695 m.str.				
2690 m.w.				
2688 m.str.				
2686 w., narr.				
2682 m.str.				
2617 v.w.				
2614 m.w.				
2606 w.				
C.	2595 v.w.	2606 w. 2595 v.w.	8 bands.	90°. 923 mm. λ.  No bands.  The rays were absorbed from about λ 2870, the Cd. line 2837 being just visible.

The rays wer then transmitted to Cd. 2265.

29 bands.

The rays were then feebly transmitted to λ 2420; the Cd. lines 2329, 2321 and 2313 were weak.

27 bands.

The absorption bands of the vapour were also photographed at a constant temperature of 15° and at the varying pressures of 736 mm., 606 mm., 456 mm., 306 mm., 156 mm., and 11 mm. The bands were similar to those described in table I at 19° and 763 mm., except that they were sharper, and, as the pressure decreased, only the stronger bands remained, so that at 11 mm. no bands were visible.

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## *m*-Dichlorobenzene.

TABLE II.

The absorption bands in the vapour of *m*-dichlorobenzene at various temperatures and pressures in a column 200 mm. long and 20 mm. diameter. Abbreviations as before.

	19°. 783 mm. λ.	30°. 807 mm. λ.	45°. 833 mm. λ.	60°. 863 mm. λ.
	2788 v.w. 2783 v.w. 2780 m.w. 2776 m.w. A 2771 m.str. 2768 str. 2764 v.w., narr. 2762 str. 2759 v.w., narr. 2756 v.w., narr.	2788 v.w. 2784 v.w. 2780 m.w. 2776 m.w. 2770 m.str. 2768 str. 2765 w., narr. 2762 str. 2759 v.w., narr. 2756 v.w., narr.	2788 v.w. 2783 v.w. 2780 m.str. 2776 m.str. 2771 m.str. 2768 m.str. 2765 v.w. 2762 str. 2759 v.w. 2756 v.w. 2754 v.w. 2752 v.w. 2746 w. 2740 m.str. 2739 v.w., narr. 2737 m.str. 2731 v.w.	No bands.  Therayswereab- sorbed from λ 2820, the Cd. lines 2748 and 2673 being visible.
B.	2752 v.w., narr. 2745 v.w. 2740 v.w. 2739 m.w. 2737 v.w. 2731 w. 2708 v.w. 2706 v.w. 2700 m.str.	2752 v.w., narr. 2745 v.w. 2741 m.w. 2738 m.w. 2737 v.w. 2731 v.w. 2709 m.w. 2706 m.w. 2700 m.w.	2731 v.w. 2709 w. and diff. 2706 w. and diff. 2700 w. and diff.	75'. 893 mm. λ.
C.	2694 str. 2690 m.str. 2685 str. 2681 m.w. 2678 v.w. 2673 v.w. 2668 v.w. 2667 w. 2665 v.w. 2660 v.w. 2657 v.w. 2640 v.w. 2631 w. 2627 w. 2618 v.w. 2616 v.w. 2610 v.w.	2694 m.str. 2690 m.str. 2685 str. 2682 w. 2678 v.w. 2673 v.w. 2668 v.w. 2667 w. 2665 v.w., narr. 2660 v.w. 2657 v.w. 2640 v.w. 2632 w. 2627 w. 2618 w. 2615 v.w. 2610 v.w.	2694 v.w. 2690 v.w. 2685 m.w. 2681 w. 2678 v.w. 2673 v.w. 2668 v.w. 2667 v.w.	No bands.  The rays were absorbed from λ 2840.
	The rays were then transmitted to λ 2665.	The rays were then transmitted to λ 2665.	The rays were then absorbed from λ 2620, the Cd. lines 2573, 2329, 2321 and 2313 being visible.	90°. 923 mm. λ.
	35 bands.	85 bands.	28 bands.	No bands.
				The rays were absorbed from λ 2870.

The absorption bands of the vapour were also photographed at a constant temperature of 15° and at varying pressures of 736 mm., 606 mm., 456 mm., 306 mm., 156 mm., and 11 mm. The bands were similar to those observed at 19° and 763 mm., except that they became sharper as the pressure decreased and only the stronger bands remained, so that at 11 mm. no bands were visible.

*o*-Dibromobenzene.

TABLE III.

The absorption bands in the vapour, of *o*-dibromobenzene at various temperatures and pressures in a column 200 mm. long and 20 mm. diameter. Abbreviations as before.

18.5°.	30°.	45°.	60°.
763 mm.	807 mm.	833 mm.	863 mm.
λ.	λ.	λ.	λ.
2778 v.w.	The bands at this temperature and pressure were similar to those observed at 18.5° and 763 mm., except that they were a little stronger.	2778 v.w.	2778 v.w.
2777 v.w.		2777 v.w.	2776 v.w.
2773 v.w.		2773 m.w.	2774 m.str.
2772 v.w.		2772 m.w.	2772 w.
2768 w.		2768 m.str.	2768 m.str.
2765 v.w.		2765 w.	2765 v.w.
A.	The rays were then absorbed from λ 2265.	2759 m.w.	2762 w.
		2758 m.str.	2759 m.str.
		2757 str.	2758 m.str.
		2752 v.w., narr.	2756 str.
		2750 m.str.	2753 w., narr.
		2724 v.w.	2750 str.
2722 v.w.	30 bands.	2722 v.w.	2718 m.w.
2717 w.		2717 m.str.	
2710 v.w.		2710 m.w.	
2700 w.		2700 m.w.	
2695 w.		2695 str.	
2690 v.w.		2690 v.w.	
2689 v.w.	2689 m.w.	2663 w.	
2686 w.	2686 str.		
2678 v.w.	2678 v.w.		
2667 v.w.	2667 v.w.		
2666 w., narr.	2666 w., narr.		
2662 w.	2662 m.str.		
2656 v.w.	2656 v.w.	The rays were then absorbed from λ 2640, the C line 2573 being visible.	
2654 w.	2654 m.w.		
2641 v.w.	2641 w.		
2640 v.w.	2640 w.		
2634 v.w.	2634 v.w.		
2630 w.	2630 w.		
The rays were then transmitted to λ 2265.	30 bands.	The rays were then absorbed from λ 2430; the Cd. lines 2321 and 2313 were just visible.	75°.
30 bands.	30 bands.	30 bands.	893 mm.
30 bands.	30 bands.	30 bands.	λ.
30 bands.	30 bands.	30 bands.	No bands
30 bands.	30 bands.	30 bands.	The rays were absorbed from λ 2810, the Cd. lines 2748 and 2573 being visible.

Experiments with the vapour at a constant temperature and varying pressures were not conducted.

*m*-Dibromobenzene.

TABLE IV.

The absorption bands in the vapour of *m*-dibromobenzene at various temperatures and pressures in a column 200 mm. long and 20 mm. diameter. Abbreviations as before.

18°		30°		45°		60°	
767 mm.		801 mm.		822 mm.		857 mm.	
λ.		λ.		λ.		λ.	
A.	2785 v.w.	The bands at this temperature and pressure were similar to those observed at 18° and 757 mm., except that they were a little stronger.		2785 v.w.		2786 v.w.	
	2782 v.w.			2782 v.w.		2781 v.w.	
	2780 v.w.			2780 v.w.		2779 v.w.	
	2778 w.			2778 m.str.		2777 m.str.	
	2774 v.w.			2774 w., narr.		2774 w., narr.	
B.	2772 w.			2772 str.		2773 str.	
	2718 v.w.			2718 v.w.		2713 v.w.	
	2710 v.w.			2710 v.w.		2710 v.w.	
C.	2706 w.			2706 m.str.		2707 m.str.	
	2705 w.			2705 w., narr.		*	
	2701 w.			2701 m.w.		2701 m.str.	
	2638 v.w.			2638 v.w.		2638 v.w.	
	2633 w.			2633 m.w.		2632 v.w.	
The rays were then transmitted to λ 2265.		than at 18° and 757 mm.		The rays were then transmitted to λ 2370, the Cd. lines 2329, 2321, and 2313 being visible		The rays were then transmitted to λ 2420.	
13 bands.		13 bands.		13 bands.		12 bands.	
						75°.	
						887 mm.	
						λ.	
						No bands.	
						The rays were absorbed from about λ 2770, the Cd. lines 2748 and 2573 being fairly strong.	
						90°.	
						917 mm.	
						λ.	
						No bands.	
						The rays were absorbed from about λ 2840; the Cd. lines 2748 and 2573 were just visible.	



Experiments with the vapour at a constant temperature and varying pressures were not conducted.

*o*-Chlorotoluene.

TABLE V.

The absorption bands in the vapour of *o*-chlorotoluene at various temperatures and pressures in a column 200 mm. long and 20 mm. diameter. Abbreviations as before.

	18°.	30°.	45°.	60°.
	756 mm.	800 mm.	826 mm.	856 mm.
	λ.	λ.	λ.	λ.
A.	2755 v.w.	The bands at this temperature and pressure were similar to those at 18° and 756 mm. and the rays were absorbed from λ 2265.	2755 w.	No bands.
	2728 v.w.		The rays were then absorbed from λ 2748, the strong Cd. lines 2573 to 2265 being visible.	The rays were absorbed from λ 2770, the Cd. lines 2329, 2321 and 2313 being visible.
	2725 v.w.			
	2724 m.w.			
	2720 m.w.			
	2719 m.str.			
	2716 v.w., narr.			
	2714 str.			
B.	2706 v.w.	23 bands.	1 band.	
	2704 v.w.			
	2696 v.w.			75°.
	2690 v.w.			856 mm.
	2686 m.w.			λ.
	2680 m.w.			No bands.
	2673 v.w.			
	2672 v.w.			
	2668 v.w.			The rays were absorbed from λ 2840, the Cd. lines 2329, 2321 and 2313 being just visible.
	2660 v.w.			
	2651 v.w.			
	2646 w.			
	2640 w.			
	2634 m.w.			
	2632 m.w.			

Therays were then transmitted to λ 2265.

23 bands.

90°.  
916 mm.  
λ.

No bands.

Therays were absorbed from λ 2850.

*m*-Chlorotoluene.—TABLE VI.

The absorption bands in the vapour of *m*-chlorotoluene at various temperatures and pressures in a column 200 mm. long and 20 mm. diameter. Abbreviations as before.

	19°.	30°.	45°.	60°.
	756 mm.	800 mm.	826 mm.	856 mm.
	λ.	λ.	λ.	λ.
I.	2749 v.w. 2737 m.w. 2736 m.w. 2794 m.w. 2793 m.w. 2717 v.w. 2711 v.w.	The bands at this temperature and pressure were similar to those observed at 19° and 756 mm., and the rays were absorbed from λ 2265, but the Cd. lines were weaker than at 19°.	No bands.	No bands.
II.	2708 m.w. 2701 m.w. 2671 v.w. 2667 v.w.		The rays were absorbed from λ 2748, but the Cd. lines 2573, 2329, 2321, 2313 and 2288 were visible.	The rays were absorbed from λ 2780; the Cd. lines 2329, 2321 and 2313 were just visible.
III.	2666 m.w. 2664 m.w. 2661 v.w.			
	2648 w.			
IV.	2640 v.w. 2635 w. 2634 w. 2598 w. 2592 w.		75°. 836 mm. λ. No bands.	90°. 916 mm. λ. No bands.
		20 bands.		
	The rays were then transmitted to λ 2265.		The rays were absorbed from λ 2810.	
	20 bands.		The rays were absorbed from λ 2830.	

*o*-Bromotoluene.—TABLE VII.

The absorption bands in the vapour of *o*-bromotoluene at various temperatures and pressures in a column 200 mm. long and 20 mm. diameter. Abbreviations as before.

	19°.	30°.	45°.	60°.	
	757 mm.	801 mm.	827 mm.	857 mm.	
	λ.	λ.	λ.	λ.	
A.	2761 v.w. 2759 v.w. 2756 v.w. 2753 v.w. 2748 v.w. 2737 v.w.	The bands at this temperature and pressure were similar to those observed at 19° and 757 mm.	2761 v.w. 2759 v.w. 2757 v.w. 2753 v.w. 2748 m.str.	No bands.	
B.	2731 v.w. 2728 v.w. 2727 v.w. 2720 m.str. 2715 m.str. 2689 v.w. 2683 v.w. 2676 v.w. 2671 m.w.		15 bands.	The rays were then absorbed from 2740; the Cd. line 2573 was visible.	The rays were absorbed from λ 2780; the Cd. lines 2748 and 2573 were just visible.
			5 bands.		
			75°.	90°.	
			887 mm.	917 mm.	
			λ.	λ.	
		No bands.	No bands.		
The rays were then transmitted to Cd. 2313.					
	15 bands.		The rays were absorbed from λ 2820.	The rays were absorbed from λ 2860.	

*m*-Bromotoluene.

TABLE VIII.

The absorption bands in the vapour of *m*-bromotoluene at various temperatures and pressures in a column 200 mm. long and 20 mm. diameter. Abbreviations as before.

	19°. 757 mm. λ.	30°. 801 mm. λ.	45°. 827 mm. λ.	60°. 857 mm. λ.	
I <sup>a</sup> .	2759 v.w. 2756 v.w. 2745 v.w. 2740 v.w.	The bands at this temperature and pressure were similar to those observed at 19° and 30°. The rays were then transmitted to λ 2288.	The bands at this temperature and pressure were similar to those at 30°. The rays were then transmitted to λ 2380.	No bands.	
II <sup>a</sup> .	2738 m.w. 2736 w. 2733 m.w. 2731 w.			The rays were absorbed from λ 2750, but the Cd. line 2673 was visible.	
	2717 v.w. 2714 v.w.				
III <sup>a</sup> .	2711 v.w. 2709 v.w. 2706 v.w. 2673 m.w. 2670 m.w.			19 bands.	75°. 887 mm. λ. No bands.
IV <sup>a</sup> .	2667 m.w. 2664 m.w. 2662 m.w. 2650 v.w.				The rays were absorbed from λ 2780, but the Cd. lines 2745 and 2573 were just visible.
			The rays were then transmitted to 2313.		
	19 bands.		90. 917 mm. λ. No bands.		
			The rays were absorbed from λ 2820.		

At the increased temperatures and pressures the bands in all the vapours became a little more diffuse; and, at the highest temperatures and pressures, the bands disappeared consequent on the overlapping general absorption. These phenomena are exactly similar to those observed in the vapours of other substances, an account of which has been given in previous communications. The groups of bands, and the number of bands, are fewer than were found in the vapours of chloro- and bromo-benzene (*loc. cit.*); and they are also fewer than those in the vapours of benzene and toluene as described by Hartley (*Phil. Trans.*, 1908, A, 209, 475). The maximum number of bands in benzene and toluene vapours were 84 and 22 respectively, and the maximum number in the vapours of chloro- and bromo-benzene were 73 and 62 respectively.

Further, Hartley divided the vapour bands of benzene into nine

groups, and those of toluene into six groups; and the author divided the bands in the vapours of chloro- and bromo-benzene into five principal groups. On comparing the bands of the vapours of *o*- and *m*-dichlorobenzene, the larger number of bands may be divided into three principal groups, but the most refrangible bands were so weak that no grouping could be attempted. These three primary groups, however, are not similar to each other, although the bands of group A are fairly comparable in both substances, and they are also comparable with the groups of bands I and II in the vapours of chloro- and bromo-benzene. Further, there is a group of bands A in *o*- and *m*-dibromobenzene which are fairly comparable with each other, and also with the group of bands A in the vapours of the corresponding dichlorobenzene compounds, and also with the bands I and II in the vapours of chloro- and bromo-benzene. The groups of bands B and C are quite different; the individual bands are wider and more diffuse, and weaker in all the disubstituted compounds. With regard to *o*-chloro- and *o*-bromo-toluene, the two groups of bands A and B are fairly comparable, and the group A is comparable with the group A of *o*- and *m*-dichloro- and dibromo-benzene. On the other hand, the four small groups into which the bands of *m*-chloro and *m*-bromo-toluene are divided are comparable in appearance with each other; but they are not comparable with any of the groups of *o*-chloro- and *o*-bromo-toluene. These four groups of the meta-compounds are a series of weak, rather closely packed bands.

At the same time it should be observed that no very close comparison of some of these bands is possible, because of the images of various bright, strong lines of cadmium which was used as the source of light. This drawback is particularly marked by the presence of the strong cadmium line 2748; and, to a less degree, by the cadmium lines 2764 and 2775. Their images overshadow the weaker bands as well as obliterate bands which are in the same neighbourhood.

#### *General Results of the Vapours.*

The general results of the preceding observations are that (1) each vapour possesses a considerable number of absorption bands which can be divided into groups; (2) these groups are comparable in appearance in the vapours of *o*- and *m*-dichloro- and dibromobenzene, where there are three primary groups; and with *o*-chloro- and *o*-bromo-toluene in which there are two primary groups; (3) the groups in *m*-chloro- and *m*-bromo-toluene are comparable with each other, but they are not comparable with the groups of bands of the other substances. The experiments were repeated several

times with two freshly prepared samples of each substance, which were redistilled several times, so that there can be no doubt about the accuracy of the differences observed in the toluene compounds; (4) the effect of introducing an atom, like chlorine or bromine, or a group of atoms like a methyl group, is to diminish the number of vapour bands; and the diminution is more marked in the case of a methyl group, although it is lighter than the halogens; (5) with increased temperature and pressures the separate bands become more diffuse.

*Solutions in Alcohol.*

Pauer (*Wied. Ann.*, 1897, **61**, 363) found three bands in alcoholic solutions of toluene; and Baly and Collie (*Trans.*, 1905, **87**, 1332) found the same number. The latter authors (*loc. cit.*) and Baly and Ewbank (*ibid.*, 1355) describe the absorption spectra of chlorobenzene and the three dichlorobenzenes and chlorotoluenes. Later Baly (this vol., p. 856) repeated the observations, and found that these substances had more absorption bands than had been previously described. The author (*loc. cit.*) has confirmed the observations, and also found that bromobenzene exhibited seven bands. These bands are comparable with each other, except that they differ in position dependent on the weights of the molecules. Further, equimolecular solutions of the substances of the present investigation have been studied; and the observed bands are completely different from those of the vapours. The solution bands are wide and diffuse, and slightly more diffuse on the less refrangible edges, and they are fewer in number than the vapour bands. It is not easy to measure the edges of the diffuse solution bands; the positions of maximum absorption are much easier to measure, and they are called the heads of the bands. The following numbers are the positions of the heads of the bands in  $M/100$ -solutions photographed through thicknesses of 4 mm.

*M/100-o-Dichlorobenzene.*

λ.

2770 f.str., wide  
2696 f.str., wide  
2615 w., wide  
2574 v.w., wide

*M/100-m-Dichlorobenzene.*

λ.

2776 f.str., wide  
2700 f.str., wide  
2621 w., wide  
2560 v.w., wide

*M/100-o-Dibromobenzene.*

λ.

2779 f.str., wide  
2710 f.str., wide  
2630 w., wide  
? 2580 v.w.

*M/100-m-Dibromobenzene.*

λ.

2780 f.str., wide  
2720 f.str., wide  
2645 w., wide  
? 2590 v.w.

*M/100-o-Chlorotoluene.*

λ.

2780 f.str., wide  
2660 v.w., wide  
‡ 2580 v.w., wide

*M/100-o-Bromotoluene.*

λ.

2745 f.str., wide  
2670 w., wide  
‡ 2595 v.w.

*M/100-m-Chlorotoluene.*

λ.

2747 f.str., wide  
2675 w., wide  
‡ 2596 v.w., wide

*M/100-m-Bromotoluene.*

λ.

2750 f.str., wide  
2680 f.str., wide  
‡ 2610 v.w.

The bands marked ‡ are very weak, and not easily distinguished. The wide diffuse solution bands of each substance are fairly comparable with the corresponding ones in the other substances: they differ only in position dependent on the weight of the substituting atoms or groups of atoms. The number of bands of the dihalogen derivatives is fewer than in the monohalogen compounds, as described before (*loc. cit.*), and there are fewer bands in the toluene compounds than in the dihalogen compounds.

*Liquids in Thin Films.*

In previous communications (Trans., 1910, **97**, 692, 1035, 1649, 1546, and this vol., p. 811) the author has given accounts of investigations of very thin films of various substances varying between thicknesses of 0.01 and 0.001 mm. Through these films general absorption only was observed. Thinner films were obtained by gently pressing a drop of the liquid between two quartz plates, and selective absorption was then noticeable. The following numbers give the heads of these liquid bands at the places of maximum absorption.

*o-Dichlorobenzene.*

λ.

2787 f.str., wide  
2702 f.str., wide  
2630 v.w., wide  
‡ 2578 vw., wide

*m-Dichlorobenzene.*

λ.

2790 f.str., wide  
2703 f.str., wide  
2635 v.w., wide  
‡ 2583 v.w., wide

*o-Dibromobenzene.*

λ.

2810 f.str., wide  
2720 f.str., wide  
2650 w., wide  
‡ 2580 v.w., wide

*m-Dibromobenzene.*

λ.

2815 f.str., wide  
2730 f.str., wide  
2655 w., wide  
‡ 2585 v.w., wide

*o-Chlorotoluene.*

λ.

2761 f.str., wide  
2676 f.str., wide  
‡ 2605 v.w., wide

*m-Chlorotoluene.*

λ.

2755 f.str., wide  
2680 f.str., wide  
‡ 2610 v.w., wide

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*o*-Bromotoluene.

$\lambda$ .  
2760 f.str., wide  
2835 w., wide  
2815 v.w.

*m*-Bromotoluene.

$\lambda$ .  
2765 f.str., wide  
2890 f.str., wide  
2820 v.w.

Pauer (*loc. cit.*) examined thin films of toluene, and found three bands. The author has also examined thin films of toluene pressed between quartz plates, and found three bands, the heads of which are:

*Toluene.*

$\lambda$ .  
2690 str., wide  
2625 str., wide  
2580 v.w., wide

All these liquid bands are wide and diffuse, and they are more diffuse on the less than on the more refrangible edges. Their general appearance is comparable with the corresponding solution bands. The bands marked ? are very weak, and not clearly distinguished.

*Discussion of Results.*

In discussing these results, the phenomena to be explained are of several kinds. First, there is the considerable number of vapour bands; secondly, the smaller number of solution bands, and of a different type; and thirdly, the smaller number of bands of the thin films which are closely comparable in appearance with the solution bands. Some explanation is also necessary to account for the diminution in the number of bands, whether in the vapours or in the thin films or in the solutions which accompanies the substitution of one or two hydrogen atoms of the benzene nucleus by a halogen atom or a methyl group.

To consider the vapours first, it may be that the vibrations of the atoms of the benzene molecule are unimpeded by any exterior forces except those which are the result of the encounters of the molecules themselves. The internal vibrations of the atoms which produce selective absorption are not subjected to any external disturbing force except those which are given to them by variations in the temperature and pressure. The general effect of these forces is apparent, not in any striking alteration in the type of each band, but in a greater diffuseness and widening. When one or more of the hydrogen atoms are replaced by a methyl group or a halogen atom, the number of vibrations in a given time is restricted with a consequent diminution in the number of the more refrangible bands. But the type of the less refrangible group is similar to the less refrangible group of bands of the original benzene molecule, and differs only in position, controlled generally by the

weight of the introduced radicle. This is true for chloro- and bromo-benzene, for *o*- and *m*-dichloro- and dibromo-benzene, and for *o*-chloro- and -bromo-toluene; but for *m*-chloro- and -bromo-toluene no such similarity exists. In these substances the orientation, the type of the inserted radicle, and the number and type of its constituent atoms, influence the nature of the selective absorption; and, in this connexion, the radiant energy of the source of light may be of paramount importance. A definite amount of energy may be absorbed, and each atom will absorb an amount dependent on its intrinsic characters and its differential relation with the other atoms of the nucleus and of the side-chains; so that space relations, as well as the number and type of the side-chains, will determine the direction of the vibrations, not only of each oriented atom or group of atoms, but also of all the atoms of the molecule, and the final adjustment will depend on the correlated oscillations or vibrations of a complex series of disturbances. In some such direction, the differences in the bands of *m*-chloro- and -bromo-toluene from those of the ortho-compounds may be explained.

When the molecules are dissolved in alcohol, their movements are considerably altered. The separate constituents of the groups of vapour bands are no longer apparent. The numerous bands have been reduced to a few large diffuse ones; and, as in the vapours, the displacement of the hydrogen atoms by methyl groups or by halogen atoms is to restrict the number of bands, and to eliminate the more refrangible bands. The author has suggested before (*loc. cit.*) that the solvent not only restrains the vibrations or oscillations of the benzene ring and its constituent atoms or side-chains by virtue of the tensional forces at the surfaces of the two types of molecules, namely, the dissolved substance and the solvent, but that it also acts as a barrier to the number of encounters, as well as an absorbent of a part of the radiant energy. The external influence of the solvent is more powerful than when the molecules are in the vaporous condition, and the total result is to modify the internal vibrations to such an extent as to alter the type of selective absorption. The number of individual bands is greatly decreased, although the characteristic broad diffuse solution bands are generally comparable with groups of the vapour bands; but they differ in position as a result of the damping force of the solvent.

In the liquids the selective absorption is only apparent in the thinnest films. The author has shown before that when the thin films were between 0.01 mm. and 0.001 mm. thick, no selective absorption was obtainable. In the later experiments, selective absorption was only obtained by pressing closely the quartz plates



binding the films. Such excessively thin films can no longer be called liquids. Their physical condition is more like that of a vapour under very high pressure; the closely packed molecules of the films must exert a tensional effect upon each other; the restraining influences on the vibrations must be very great; and the selective absorption approximates towards the conditions implied by a solution or by a vapour under very high pressure. The result is exhibited in the appearance of wide diffuse bands not unlike those of the solutions; and the greater shift of the bands towards the red end is caused by the closely packed molecules interfering with the rate of vibration.

The author is engaged in a comparative study of the corresponding iodine compounds and of other compounds of benzene and toluene; and he has again to thank the Government Grant Committee of the Royal Society, by whose assistance the greater part of the cost of the apparatus used in the investigation was defrayed.

UNIVERSITY CHEMICAL LABORATORY,  
CAMBRIDGE.

## CXCII. — *Substances Related to Cochenillic and Carminic Acids. Part I. Synthesis of the Methyl Ether of $\beta$ - and of $\gamma$ -Coccinic Acid.*

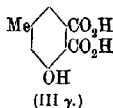
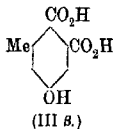
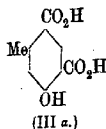
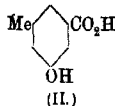
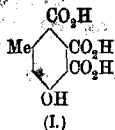
By ANDREW NORMAN MELDRUM (late Carnegie Research Fellow).

THE discovery of cochenillic acid and the establishment of its constitution form an important addition to our knowledge of the colouring matter contained in cochineal. Liebermann and Voswinckel discovered the acid amongst the oxidation products of cochineal-extract and of carminic acid (*Ber.*, 1897, **30**, 688), and by a study of its degradation products they proved it to have the constitution represented in formula I (*Ber.*, 1897, **30**, 1733).

### *Constitution of the Degradation Products of Cochenillic Acid.*

Liebermann and Voswinckel found that cochenillic acid, when heated under various conditions, yields three other acids, two of which are identical with substances already known. One of them proved to be 5-hydroxy-*m*-toluic acid (II), whilst another,  $\alpha$ -coccinic acid, as they named it, is identical with *m*-hydroxyuvitic acid (III a). The third degradation product was a new substance, and was called

$\beta$ -coccinic acid. It has the constitution shown in formula III  $\beta$ , although, as a hydroxyphthalic acid derived from cochenillic acid,

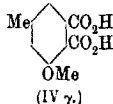
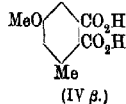


it might equally well have the formula III  $\gamma$ . It does not, however, give a distinct colour-reaction with ferric chloride, as a substance of that type ought to do. The constitution of the  $\beta$ -acid being thus a settled matter, the name  $\gamma$ -coccinic acid can be assigned to the substance (hitherto unknown) of formula III  $\gamma$ .

#### Synthesis of Substances Related to Cochenillic Acid.

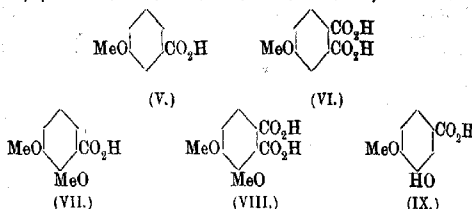
5-Hydroxy-*m*-toluic acid has been obtained from *m*-toluic acid by Jacobsen (*Ber.*, 1881, **14**, 2357), and from ethyl acetoneoxalate by Claisen and Miller (*Ber.*, 1889, **22**, 3272).<sup>\*</sup> *m*-Hydroxyuvitic acid has been synthesised by Oppenheim and Pfaff (*Ber.*, 1874, **7**, 929; 1875, **8**, 884), Oppenheim and Precht (*Ber.*, 1876, **9**, 321), Claisen (*Annalen*, 1897, **297**, 43), and Errera (*Ber.*, 1899, **32**, 2785). These syntheses were carried out without any explicit intention of obtaining substances related to carminic or cochenillic acid. In the present paper the author gives an account of an attempt to synthesise  $\beta$ -coccinic acid. The starting point of the work is the substance 5-hydroxy-*m*-toluic acid, which, it may be emphasised here, can be obtained, on the one hand, by the degradation of carminic acid, and, on the other, by synthesis from acetone and ethyl oxalate.

The work actually accomplished has resulted in the synthesis of two isomeric substances, one of which is the methyl ether (IV  $\beta$ ) of the intended acid, whilst the other, from the nature of the synthetic method employed, can have only the constitution IV  $\gamma$ , that is, it is the methyl ether of  $\gamma$ -coccinic acid.

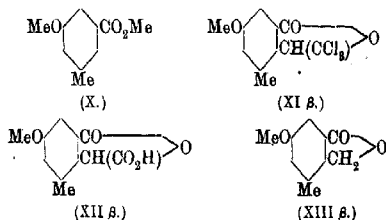


<sup>\*</sup> The second synthesis was elucidated by J. Bishop Tingle (*Diss.*, München, 1889).

These two substances, IV  $\beta$  and IV  $\gamma$ , are methoxyphthalic acids, and a method of synthesising such acids is due to Fritsch. The net result of the method is to introduce a second carboxyl group in the ortho-position with respect to a carboxyl group already in the molecule, and in the para-position to a methoxy-group. Thus *m*-methoxybenzoic acid (V) leads to 4-methoxyphthalic acid (VI), whilst 2:3-dimethoxybenzoic acid (VII) furnishes hemipinic acid (VIII) (*Annalen*, 1897, **296**, 358; 1898, **301**, 360):



The series of reactions involved in Fritsch's synthesis is well exemplified in the case of  $\beta$ -coccinic acid. 5-Hydroxy-*m*-toluic acid is converted into the methyl methoxy-ester (X), and this, in the presence of sulphuric acid, condenses with chloral, with production of 5-methoxy-3-methyl-2-trichloromethylphthalide (XI  $\beta$ ). The latter, on hydrolysis, gives 5-methoxy-3-methylphthalide-2-carboxylic acid (XII  $\beta$ ), which, when heated, loses carbon dioxide, forming 5-methoxy-3-methylphthalide (XIII  $\beta$ ). This phthalide, on oxidation, yields 5-methoxy-3-methylphthalic acid (IV  $\beta$ ), that is, the methyl ether of  $\beta$ -coccinic acid:



So far, the synthesis proved a success. It was found impracticable, however, to obtain  $\beta$ -coccinic acid by hydrolysis of the methyl ether. Treatment in the usual way with hydriodic acid resulted in a large yield of 5-hydroxy-*m*-toluic acid. Presumably  $\beta$ -coccinic acid was formed, and was decomposed by the hydriodic acid. This is in accordance with the known behaviour of certain hydroxyphthalic acids on treatment with hydriodic or hydrochloric acid: the tendency is to the formation of a *m*-hydroxybenzoic acid. 3-Hydroxyphthalic

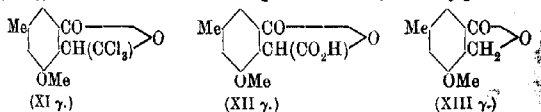
acid (Rees, *Ann.*, 1838, 233, 234) and 2-hydroxyterephthalic acid (Burkhardt, *Ber.*, 1877, 10, 145) give *m*-hydroxybenzoic acid in each case, whilst camipinic acid (VIII) gives isovanillic acid (IX) (Wegscheider, *Sitzungsber. K. Akad. Wiss. Wien*, 1882, 85, 963, 968).

For purposes of identification, therefore, the methyl ether of  $\beta$ -coccinic acid was prepared from cochenillic acid. This specimen, of natural origin, was found by the "mixed melting-point" method to be as nearly as possible the same as the synthetic substance, and the corresponding anhydrides proved unquestionably the same.

### *$\gamma$ -Coccinic Acid.*

A complication arose in the course of the synthesis just described: hydrolysis of the trichloromethylphthalide produced, not one, but two carboxylic acids. The two acids are not only isomeric with one another, but very similar in chemical behaviour: each, when heated, gives a phthalide, and each phthalide, on oxidation, gives a phthalic acid. The explanation of this, which seems the most likely one, is, that the trichloromethylphthalide is really a mixture of two isomeric substances, namely, 5-methoxy-3-methyl-2-trichloromethylphthalide (XI  $\beta$ ) and 3-methoxy-5-methyl-2-trichloromethylphthalide (XI  $\gamma$ ). The assumption here is that chloral condenses with the methyl methoxytoluate in the ortho- as well as in the para-position with respect to the methoxy-group, and that there results a mixture of two trichloromethylphthalides, which, being isomorphous with one another, cannot be separated by crystallisation. There is nothing intrinsically impossible in the supposition that condensation can occur in both positions, although Fritsch observed no instance of it in his work.

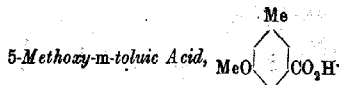
Hydrolysis of 3-methoxy-5-methyl-2-trichloromethylphthalide (XI  $\gamma$ ) must give 3-methoxy-5-methylphthalide-2-carboxylic acid (XII  $\gamma$ ). The acid, when heated, gives 3-methoxy-5-methylphthalide



(XIII  $\gamma$ ), and the latter on oxidation yields 3-methoxy-5-methylphthalic acid (IV  $\gamma$ ), the methyl ether of  $\gamma$ -coccinic acid.

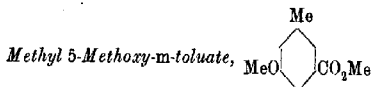
As a basis for further work,  $\gamma$ -coccinic acid is of unusual importance. By subjecting it, for instance, to chemical changes similar to those employed for obtaining  $\beta$ -coccinic acid, of course with suitable modifications, one might expect to obtain synthetic cochenillic acid.

## EXPERIMENTAL



The 5-hydroxy-*m*-toluic acid required for this investigation was synthesised from acetone and ethyl oxalate much according to details given by Tingle (*loc. cit.*) and by Meldrum and Perkin (*Trans.*, 1909, **95**, 1896). The hydroxy-acid was converted into the methoxy-acid by methyl sulphate in the usual way. A small amount of the product was recrystallised from glacial acetic acid; it separated in needles, and melted at  $134^\circ$ . Titration with standard alkali showed that it was the expected substance.

0.0973 neutralised 5.89 c.c. 0.1*N*-sodium hydroxide solution, or 0.02356 NaOH, whilst this amount of the acid  $\text{C}_9\text{H}_{10}\text{O}_3$  should neutralise 0.02345.



The methoxy-acid (56 grams) was dissolved in methyl alcohol (180 c.c.), and, after the addition of sulphuric acid (8 c.c.), the solution was boiled under a reflux condenser during four hours. The product was cooled, dissolved in ether, and washed with water so as to remove all sulphuric acid and methyl alcohol. The ethereal solution was dried, and distilled. The ester boiled at  $262\text{--}263^\circ/752\text{ mm}$ . Yield, 52 grams. As a check, the crude ester was analysed:

0.1446 gave 0.3521  $\text{CO}_2$  and 0.0830  $\text{H}_2\text{O}$ .  $\text{C}=66.4$ ;  $\text{H}=6.4$ .  
 $\text{C}_{10}\text{H}_{12}\text{O}_3$  requires  $\text{C}=66.7$ ;  $\text{H}=6.7$  per cent.

*5-Methoxy-3-methyl-2-trichloromethylphthalide* (XI  $\beta$ ) and  
*3-Methoxy-5-methyl-2-trichloromethylphthalide* (XI  $\gamma$ ).

Methyl 5-methoxy-*m*-toluate (10 grams), chloral hydrate (10 grams), and sulphuric acid (50 c.c.) were mixed together, when heat was evolved, and the materials formed a clear solution. After twenty-four hours the solution was diluted with water, when a heavy liquid separated and soon became solid. The solid was collected, washed with 50 per cent. alcohol, and dried. The yield was 15 grams.

The substance was crystallised from methyl alcohol. When pure it is white, and melts at  $116\text{--}117^\circ$ . The crystals have the shape of

oblique double pyramids, passing into rectangular plates with the corners truncated:

0.2037 gave 0.2968 AgCl.  $\text{Cl} = 36.0$ .

$\text{C}_{11}\text{H}_9\text{O}_5\text{Cl}_3$  requires  $\text{Cl} = 36.0$  per cent.

The product of the above condensation, having been found on hydrolysis to give rise to two isomeric acids, may possibly itself consist of a mixture of two isomeric trichloromethylphthalides. The material was therefore crystallised repeatedly from various solvents, namely, acetone, acetic acid, methyl alcohol, and ether, and in this way a solid which melted at  $117^\circ$  was obtained. This on hydrolysis was found to yield two acids as before. It is therefore impracticable to separate the two isomeric trichloromethylphthalides, of which it probably consists, by crystallisation.

*Hydrolysis of the Trichloromethylphthalides. Preparation of 5-Methoxy-3-methylphthalide-2-carboxylic Acid (XII β).*

Numerous experiments were made in order to ascertain the best way of hydrolysing the trichloromethylphthalides, and in the end the following process was adopted. The phthalide (15 grams) in a state of fine powder was added to about its own weight of alcohol, the mixture was heated until the alcohol began to boil, and then the hot pasty mass was added to a solution of sodium hydroxide (15 grams) in water (75 c.c.). Heat was evolved, and the alkaline solution was cooled so as to keep the temperature at  $50-60^\circ$ . The phthalide dissolved almost completely, and the solution became dark in colour.

Minute crystals were formed in the solution, of a substance which proved to be a sodium salt. It was collected, dissolved in water, and purified by boiling with animal charcoal. The free acid, obtained by acidifying the solution of this sodium salt, is a white substance, which, when pure, melts at  $170^\circ$ . From acetone it crystallises in prisms and plates with oblique ends. For analysis it was crystallised from acetic acid, and finally from water.

0.2575 neutralised 11.68 c.c. 0.1N-sodium hydroxide solution, or 0.0467 NaOH, whilst this amount of the acid  $\text{C}_{11}\text{H}_{10}\text{O}_5$  should neutralise 0.0464:

0.1285 gave 0.2781  $\text{CO}_2$  and 0.0521  $\text{H}_2\text{O}$ .  $\text{C} = 59.0$ ;  $\text{H} = 4.51$ .

$\text{C}_{11}\text{H}_{10}\text{O}_5$  requires  $\text{C} = 59.5$ ;  $\text{H} = 4.5$  per cent.

The calcium salt is characteristic; it is much less soluble than the barium or potassium salt, and it crystallises in warts, of the composition  $(\text{C}_{11}\text{H}_9\text{O}_5)_2\text{Ca} \cdot 3\text{H}_2\text{O}$ . When heated it seems to decompose, for concordant figures for the water of crystallisation could not be obtained:

0.1857 gave 0.0472  $\text{CaSO}_4$ .  $\text{Ca} = 7.45$ .

0.1598 „ 0.0402  $\text{CaSO}_4$ .  $\text{Ca} = 7.40$ .

$(\text{C}_{11}\text{H}_9\text{O}_5)_2\text{Ca} \cdot 3\text{H}_2\text{O}$  requires  $\text{Ca} = 7.46$  per cent.

The constitution of the acid is shown by the fact that it can be converted by a series of changes into the methyl ether of  $\beta$ -coccinic acid. Hence it is 5-methoxy-3-methylphthalide-2-carboxylic acid, and the isomeride produced at the same time must be 3-methoxy-5-methylphthalide-2-carboxylic acid.

#### 5-Methoxy-3-methylphthalide (XIII $\beta$ ).

The phthalidecarboxylic acid of m. p.  $170^\circ$  (6 grams) along with naphthalene (20 grams) was heated at  $180$ – $190^\circ$  until the evolution of carbon dioxide ceased. The residue was then distilled in a current of steam in order to remove naphthalene, care being taken not to continue the operation unduly, because the phthalide is somewhat volatile with steam. It crystallises from water or acetone in colourless needles or slender prisms, melting at  $105.5^\circ$ :

0.1068 gave 0.2636  $\text{CO}_2$  and 0.0554  $\text{H}_2\text{O}$ .  $\text{C} = 67.3$ ;  $\text{H} = 5.8$ .

$\text{C}_{10}\text{H}_{10}\text{O}_5$  requires  $\text{C} = 67.4$ ;  $\text{H} = 5.6$  per cent.

#### 5-Methoxy-3-methylphthalic Acid (IV $\beta$ ).

The phthalide just described (3.2 grams) was dissolved in dilute potassium hydroxide solution, and to this was added a solution of potassium permanganate (3.8 grams) in water (100 c.c.). After about twelve hours the hydrated oxide of manganese was removed by filtration, and the filtrate was acidified and extracted with ether. The ethereal extract gave on evaporation a white solid, which was an acid; it was crystallised from acetic acid and then from water, when it melted and effervesced at  $184^\circ$ .

0.1306 neutralised 12.46 c.c. 0.1*N*-sodium hydroxide, or 0.04984  $\text{NaOH}$ , whilst this amount of the dibasic acid,  $\text{C}_{10}\text{H}_{10}\text{O}_5$ , ought to neutralise 0.04975  $\text{NaOH}$ :

0.1459 gave 0.3061  $\text{CO}_2$  and 0.0641  $\text{H}_2\text{O}$ .  $\text{C} = 57.2$ ;  $\text{H} = 4.9$ .

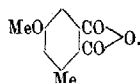
$\text{C}_{10}\text{H}_{10}\text{O}_5$  requires  $\text{C} = 57.1$ ;  $\text{H} = 4.8$  per cent.

For the purpose of comparison with the synthetic substance, the methyl ether of  $\beta$ -coccinic acid was prepared from cochenillic acid. Cochenillic acid (3 grams) was heated at  $255$ – $260^\circ$  until the evolution of carbon dioxide ceased. The cold residue, which was crystalline, was dissolved in acetone, and the addition of benzene to the solution caused the formation of a brown precipitate, which was removed by filtration. The filtrate was evaporated, and the solution gave crystals which melted at  $168^\circ$  (m. p. of  $\beta$ -coccinic

anhydride 186–183° (Liebermann and Voswinckel). The yield was 1.4 grams.

In order to obtain the methyl ether of  $\beta$ -coccinic acid, the anhydride (1.4 grams) was dissolved in potassium hydroxide, and methylated by the addition of methyl sulphate (2 c.c.) in the usual way. The solution having been acidified and the acid product isolated by means of ether, the acid was crystallised from water and then again from ether. It melted at 179°, and had a yellow tinge. The identity of this substance with the synthetic product was tested by the "mixed melting-point" method. The synthetic product melted at 184°, and the mixture at 183°, the temperature being raised rapidly. It must be noted that this "melting-point" is really the temperature of rapid conversion of a phthalic acid into its anhydride, and can be altered, for instance, by altering the rate of heating.

5-Methoxy-3-methylphthalic Anhydride,



The anhydride was prepared by heating the phthalic acid very carefully. The product having been dissolved in hot benzene, it separated in wisps of needles.

0.1095, dissolved in water (50 c.c.), neutralised 11.37 c.c. 0.1N-sodium hydroxide solution, or 0.04548 NaOH, whilst this amount of phthalic anhydride,  $C_{10}H_6O_4$ , ought to neutralise 0.04562 NaOH.

The synthetic anhydride melted at 139°. There was only enough of the anhydride made from cochenillic acid for the "mixed melting-point" test. The mixture melted at 138°.

### 3-Methoxy-5-methylphthalide-2-carboxylic Acid (XII $\gamma$ ).

The trichloromethylphthalides having been hydrolysed, and the precipitated sodium salt separated, as described on p. 1717, the filtrate was treated with acid, so as to leave it faintly alkaline, and then boiled to remove alcohol. The solution was acidified, and the resulting precipitate was crystallised once from glacial acetic acid.

The material thus obtained is a mixture of two isomeric organic acids, and the separation of the two was carried out by means of the calcium salts. The mixture was dissolved in ammonium hydroxide, and then calcium chloride solution was added. First the calcium salt of 5-methoxy-3-methylphthalide-2-carboxylic acid separated in warts, and finally, from the concentrated mother



liquors, the calcium salt of 3-methoxy-5-methylphthalide-2-carboxylic acid in silky needles. The free acid obtained from this calcium salt is a white substance, which crystallises from acetone in short, stout, oblique prisms. For analysis it was crystallised from acetic acid and then from water. It melts at  $190^{\circ}$ .

0.1853 neutralised 8.36 c.c. 0.1*N*-sodium hydroxide solution, or 0.03344 NaOH, whilst this amount of the acid  $C_{11}H_{10}O_5$  ought to neutralise 0.03339:

0.1355 gave 0.2928  $CO_2$  and 0.0553  $H_2O$ .  $C=58.9$ ;  $H=4.53$ .  
 $C_{11}H_{10}O_5$  requires  $C=59.5$ ;  $H=4.5$  per cent.

The calcium salt was analysed. As in the case of the calcium salt of the isomeric acid, concordant figures for the water of crystallisation were not obtained:

0.1779 gave 0.0440  $CaSO_4$ .  $Ca=7.28$ .

$(C_{11}H_9O_5)_2Ca \cdot 3H_2O$  requires  $Ca=7.46$  per cent.

### 3-Methoxy-5-methylphthalide (XIII $\gamma$ ).

3-Methoxy-5-methylphthalide-2-carboxylic acid (9 grams) along with naphthalene (27 grams) was heated at  $180-190^{\circ}$  until the evolution of carbon dioxide ceased. The naphthalene having been removed by distillation in a current of steam, the residue was crystallised from acetone, and then from alcohol, from which it separated in yellow, minute scales, melting at  $135.5^{\circ}$ :

0.1351 gave 0.3318  $CO_2$  and 0.0684  $H_2O$ .  $C=67.0$ ;  $H=5.6$ .  
 $C_{10}H_{10}O_5$  requires  $C=67.4$ ;  $H=5.6$  per cent.

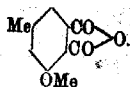
### 3-Methoxy-5-methylphthalic Acid (IV $\gamma$ ).

The phthalide just described (10 grams) was dissolved in potassium hydroxide solution, and then a solution of potassium permanganate (12 grams) in water (400 c.c.) was added. After about twelve hours the hydrated oxide of manganese was removed, the solution was rendered faintly alkaline, evaporated to small bulk, and acidified. The free acid was purified by crystallisation from glacial acetic acid, and then from acetone; it consists of colourless, minute crystals, and melts and effervesces at  $200^{\circ}$ .

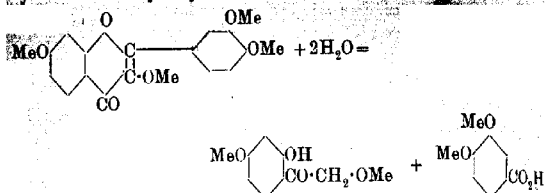
0.0609 neutralised 5.82 c.c. 0.1*N*-sodium hydroxide solution, or 0.02328 NaOH, whilst this amount of the dibasic acid,  $C_{10}H_8O_5$ , ought to neutralise 0.02320:

0.1297 gave 0.2713  $CO_2$  and 0.0576  $H_2O$ .  $C=57.05$ ;  $H=4.9$ .  
 $C_{10}H_8O_5$  requires  $C=57.1$ ;  $H=4.8$  per cent.

**3-Methoxy-5-methylphthalic Anhydride.**

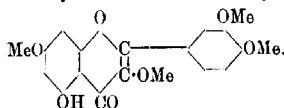


fisetin tetramethyl ether is digested with boiling alcoholic potassium hydroxide it is hydrolysed according to the following scheme:



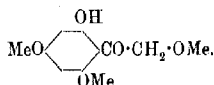
with formation of veratric acid and fisetol dimethyl ether, and, indeed, fisetin is the first compound to which a flavonol constitution was assigned.

When, however, quercetin tetramethyl ether, the fullest methylation product of quercetin which could be obtained by the employment of methyl iodide, was similarly treated (Herzig,



*Monatsh.*, 1888, **9**, 552), veratric acid and a syrupy phloroglucinol derivative, subsequently identified as phloroglucinol monomethyl ether (*Trans.*, 1902, **81**, 471), were produced. Myricetin pentamethyl ether behaved similarly, with production of gallic acid, trimethyl ether, and phloroglucinol monomethyl ether.

More recently it has been shown by Waliaschko (*Arch. Pharm.*, 1904, **242**, 242) that quercetin pentamethyl ether can be prepared by means of methyl sulphate, and Herzig (*Ber.*, 1909, **42**, 155) has now found that this completely methylated compound is hydrolysed by alcoholic potassium hydroxide in an analogous manner to fisetin tetramethyl ether, with production of veratric acid and *o*-hydroxy-fisetol trimethyl ether (6-hydroxy-2:4-dimethoxyphenyl methoxy-methyl ketone):



An interesting point in connexion with myricetin (*loc. cit.*) is the fact that, although methyl iodide gives only a pentamethyl derivative, ethyl iodide, on the other hand, furnishes the hexaethyl compound, for with other members of the flavonol group no fully ethylated derivatives have been hitherto produced by this method. During the previous investigation the action of alcoholic potassium

hydroxide of the potassium was studied with unsatisfactory results, in that the anticipated hydroxyfisetol triethyl ether did not appear to be formed as a result of the hydrolysis. As, however, it seemed possible that the difficulty may have arisen from the fact that but a very meagre quantity of the myricetin hexaethyl ether was available for the experiments, or from a too prolonged action of the alkali, it was desirable to re-investigate this point with a larger quantity of the substance, and simultaneously to study the hitherto unknown myricetin hexamethyl ether in this respect.

#### EXPERIMENTAL.

The following method was employed for the preparation of myricetin from the *Myrica nagi* extract. Four hundred grams of the material were dissolved in 6 litres of hot water, the solution treated with 400 c.c. of hydrochloric acid (33 per cent.), and heated to the boiling point for two hours, in order to hydrolyse the glucoside myricitrin. When cold, the deep brown precipitate was collected, dried at the ordinary temperature, and extracted with alcohol. The extract, when evaporated to a small bulk and cautiously treated while hot with a little boiling water, became semi-solid, owing to the separation of crude myricetin, which was removed by filtration, and washed with dilute alcohol. Yield, 37 grams. For purification, and more especially with the object of removing a trace of a second colouring matter, probably quercetin, which is present, the product was acetylated, and the acetyl derivative crystallised from a mixture of acetic acid and alcohol until it melted at 211—212°. It was subsequently hydrolysed with alkali in the usual manner, with the production of approximately 20 grams of pure myricetin.

Experiment indicated that myricetin hexamethyl ether can be readily prepared by treating the dry potassium salt of the pentamethyl compound with cold methyl sulphate. Waliaschko (*loc. cit.*) employed this method successfully in the preparation of quercetin pentamethyl ether from the trimethyl ether, and the same process with certain modifications was subsequently adopted by Watson (*Proc.*, 1911, 27, 163). The product of the reaction was washed with ether, digested with hot water, and crystallised from alcohol with the aid of animal charcoal.

On the other hand, myricetin can also be fully methylated by treating its solution in methyl alcohol with a large excess of alkali and methyl sulphate, as suggested by Herzig (*loc. cit.*) in the case of quercetin. On keeping, myricetin hexamethyl ether does not separate, but is gradually deposited when the concentrated alcoholic solution is diluted with water.

Found: C=62.69; H=5.30; Me=21.96.

$C_{15}H_{14}O_2(OMe)_6$  requires C=62.68; H=5.47; Me=23.38 per cent.

When slowly crystallised from alcohol it separates in prismatic needles, but by rapidly cooling the hot concentrated solution, as a colourless, woolly mass of fine needles resembling quercetin pentamethyl ether. It melts at 154–156°, and is sparingly soluble in cold alcohol.

In order to study the products of the hydrolysis of myricetin hexamethyl ether, 5 grams of the substance were digested with a boiling solution of 10 grams of potassium hydroxide in 50 c.c. of 80 per cent. alcohol for seven hours. The hot liquid, which on cooling became semi-solid owing to the separation of a potassium salt, was evaporated to dryness, treated with water, and the solution filtered from a trace of insoluble matter. On passing carbon dioxide into this solution, colourless crystals separated in considerable amount, and when these had been removed (2.18 grams), the filtrate yielded to ether a further quantity of the same compound (0.34 gram). It was purified by crystallisation from alcohol. (Found, C=58.36; H=6.39; Me=19.45. Calc., C=58.41; H=6.19; Me=19.91 per cent.) It consisted of colourless, prismatic needles, and appeared to be identical with the *o*-hydroxyfisetol trimethyl ether which Herzig obtained from quercetin pentamethyl ether, in that it melted at 102–104°, and the oxime which was prepared from it at 146–148°.

Being in possession of some quercetin tetramethyl ether, this was converted into the pentamethyl compound by Waliaschko's method (an operation which proceeds quite as smoothly as when the trimethyl ether is employed), and from this hydroxyfisetol trimethyl ether was prepared. A mixture of this substance and that produced from myricetin hexamethyl ether melted at 102–104°. The mother liquors obtained when the crude hydroxyfisetol trimethyl ether was crystallised from alcohol contained a trace of a second compound, which could be only isolated as a viscid, readily soluble mass, and apparently consisted of crude phloroglucinol dimethyl ether.

The sodium bicarbonate solution from which the hydroxyfisetol trimethyl ether had been isolated gave, on neutralisation with acid, a colourless, crystalline precipitate (2.05 grams), and when this had been removed the filtrate yielded to ether a small quantity of the same substance (0.401 gram). It crystallised from water in needles, melting at 167–169°, and consisted of gallic acid trimethyl ether. (Found, C=56.64; H=5.57. Calc., C=56.61; H=5.66 per cent.) These results therefore rendered it fairly evident that myricetin hexaethyl ether should, when hydrolysed with boiling alcoholic potassium hydroxide under suitable conditions, yield, not only the

gallic acid triethyl ether previously obtained (*loc. cit.*), but also a hydroxyfisetol triethyl ether corresponding with the methyl compound above described.

Myricetin hexaethyl ether was prepared by treating a boiling solution of 14.5 grams of myricetin in 200 c.c. of alcohol and 70 c.c. of ethyl iodide with 28 grams of potassium hydroxide in alcohol drop by drop during two days. The product isolated as usual consisted of the almost pure ether (9.6 grams), which, after recrystallisation, melted at 149—151°.

When submitted to the action of boiling alcoholic potassium hydroxide under identical conditions to those employed with the methyl compound, myricetin hexamethyl ether yielded a solution which, when evaporated, gave a residue soluble in water. On passing carbon dioxide into the solution, a crystalline precipitate separated in considerable amount, and this, after being collected and crystallised from alcohol, was obtained in colourless, prismatic needles, melting at 96—97°. The analyses of this compound indicated that it had, as was anticipated, the composition of a *hydroxyfisetol triethyl ether*.

Found: C=62.66, 62.49; H=7.87, 7.61.

$C_{14}H_{20}O_5$  requires C=62.68; H=7.46 per cent.

The alcoholic mother liquors resulting from the purification of this compound contained a second product isolated as a transparent, viscid mass, which probably consisted of impure phloroglucinol diethyl ether. It is accordingly evident that the hydroxyfisetol triethyl ether to some extent suffers hydrolysis in the presence of boiling alcoholic potassium hydroxide, and the unsuccessful attempt to prepare it from myricetin hexaethyl ether in the former experiment can be therefore accounted for by the too prolonged action of the reagent.

As the result of this investigation there can be no doubt that myricetin is a hydroxyquercetin, and possesses the constitution given at the commencement of this paper. An attempt is in progress to synthesise myricetin by the employment of the degradation products of its hexamethyl ether (hydroxyfisetol trimethyl ether and gallic acid trimethyl ether), and the results of this work will, it is hoped, be shortly communicated to the Society.

CLOTHWORKERS RESEARCH LABORATORY,  
THE UNIVERSITY, LEEDS.

## CXCIV.—*The Photochemical and Thermal Interaction of Chlorine and Carbon Monoxide.*

By DAVID LEONARD CHAPMAN and FRANK HOUGHTON GEE.

IN previous communications published by one of us in conjunction with C. H. Burgess and P. S. MacMahon on the photochemical interaction of chlorine and hydrogen, it has been postulated that the agency whereby the union of the gases is brought about is the evanescent forms of energy acquired by the molecules of the system from the visible light extinguished by the chlorine in virtue of the selective absorption exhibited by that gas. That the extinction of visible light by a sensitive mixture of chlorine and hydrogen is not greater than that resulting from the selective absorption of the chlorine, and that therefore the so-called photochemical extinction is an imaginary phenomenon, has been established by experiment (Burgess and Chapman, *Trans.*, 1906, **89**, 1433). As this experimental result is of fundamental importance, so far as the theory of photochemical change is concerned, we may draw attention to the fact that Winther in his recent interesting work on Eder's solution (*Zeitsch. wiss. Photochem.*, 1910, **8**, 242) arrives at a similar conclusion. After conducting an experimental investigation on the point in question, he remarks: "Nach diesem Ergebnisse, mit den Resultaten von Burgess and Chapman (für chlorknallgas) und von Lemoine (für Ferrioxalat) zusammengehalten, scheint mir der Begriff der photochemischen Extinction, in seiner bisherigen Bedeutung aus der wissenschaftlichen Photochemie ausscheiden zu müssen." Concerning the mechanism of the photochemical changes under consideration, our own view is briefly this. Chlorine, when it is absorbing light, preserves, for a time, the transformed light energy in efficient forms which are gradually changed, and finally become the ordinary heat energy of the system, the rate of degradation being considerably greater in the presence of certain impurities. This efficient energy confers on the gas the property of reacting with other substances for which it possesses an affinity, and therefore the presence of those impurities which hasten the degradation of energy is a circumstance that can only result in a reduction in the rate of a possible photochemical change.

It might be urged that if efficient energy is accumulated in the chlorine in the manner assumed, and that if consequently the light is not instantly degraded to the state in which it exists in the unilluminated system at the same temperature, it ought to be possible to demonstrate the existence of this energy in the illumin-

ated gas by some physical means. The work of R. W. Wood on the resonance spectra of the elements would appear to have a direct bearing on this aspect of the question. Five years ago it was shown by this investigator that iodine—an element allied to chlorine—in the state of vapour emits a green light when the rays from an arc lamp act on it, and that in the presence of small quantities of oxygen the fluorescent light is considerably reduced in intensity. At that time an unsuccessful attempt was made to show that chlorine would fluoresce under similar conditions. Quite recently Wood has returned to the subject (*Phil. Mag.*, 1911, [vi], 21, 261, 309, and 314), and his latest results are such as to strengthen the conviction that there is a close relationship between the phenomena investigated by him and those observed in the study of photochemistry. He has now shown that, when the pressure is sufficiently low, bromine vapour can be made to fluoresce, a fact which very considerably increases the probability that chlorine, exposed to light rays, will ultimately be shown to be capable of retaining the absorbed energy in an efficient form for a sufficient length of time to give rise to the phenomenon of fluorescence. What is still more significant is the influence of impurities on the fluorescence of iodine vapour. When the vapour is excited by monochromatic light—the green line of mercury—and the fluorescent light is analysed, it has been found to consist of a number of lines, designated by Wood a resonance spectrum. The line spectrum becomes a band spectrum when helium is present in the vapour, and at the same time the proportion of light in the red to that in the green is increased. The helium transforms and simultaneously degrades the energy. Wood also finds that after the iodine vapour has been mixed with the electronegative gases chlorine or oxygen, the degradation is so rapid that the fluorescence can no longer be made manifest. Now all the gases which retard or prevent the interaction of chlorine and hydrogen are likewise electronegative in character. This close coincidence would be most remarkable if merely fortuitous, but if, as we are disposed to think, it arises from a causal connexion between the two classes of phenomena, it could scarcely be disputed that it does afford strong presumptive evidence in favour of the view that photochemical inhibition results from the property possessed by the inhibitor of degrading the energy essential to the progress of the chemical change. The fact (for which this communication contains evidence) that the gases which behave as inhibitors towards the action between chlorine and carbon monoxide are also inhibitors in the case of the interaction of chlorine and hydrogen, lends further support to the same view.

We may here offer a few remarks on the views published by



Weigert (*Ann. Physik*, 1907, [iv], **24**, 55 and 243) on the mechanism of photochemical changes. Weigert finds that although visible light hastens both the decomposition of carbonyl chloride and the combination of chlorine and carbon monoxide at temperatures ranging between 450° and 510°, it is incapable of altering the percentage composition of a mixture of chlorine, carbon monoxide, and carbonyl chloride in thermal equilibrium. Basing his views on this fact, he argues that the action of the light is merely catalytic in its nature, and he maintains that there is produced, under the action of light, a catalyst in the form of molecular complexes ("Reaktionskerne"), the influence of which on the chemical change may be compared with that of the microscopic particles of platinum in a colloidal solution of that metal on the decomposition of hydrogen peroxide. The theory does not commend itself to us for two reasons, which are: (a) the want of any independent evidence for the existence of reaction nuclei in the illuminated system, (b) its necessary limitation, in its present form, to that class of photochemical changes in which there is no accumulation of available energy. Coehn and Becker (*Ber.*, 1910, **43**, 130) have shown that carbonyl chloride is appreciably decomposed into chlorine and carbon monoxide by the very refrangible ultraviolet rays emitted by a quartz mercury lamp, at a temperature considerably below that at which the concentration of the products of dissociation of carbonyl chloride in thermal equilibrium with the vapour of carbonyl chloride is sufficiently great to be capable of being measured, and they have pointed out that the statement on which Weigert bases his views that the equilibrium between carbonyl chloride and its products of decomposition is uninfluenced by light, is not therefore generally true. We are not aware, however, of any ascertained facts connected with the union of chlorine with hydrogen or carbon monoxide in visible light actually inconsistent with Weigert's hypothesis, which may consequently be still held as an alternative explanation of a limited class of photochemical changes.

For the investigation of some questions the action between chlorine and carbon monoxide possesses advantages over that between chlorine and hydrogen. The union of the former gases is accompanied by a contraction, and therefore the course of the change can be followed without water being present. The absence of water, besides making it possible to perform experiments at high temperatures, is also a distinct advantage in the investigation of the effects of those inhibitors which dissolve in, or are acted on by, this liquid. Thus, owing to the solubility of nitrosyl chloride in water, the influence of this inhibitor on the photochemical interaction of chlorine and hydrogen could not be investigated so

completely as was desirable, whereas with a mixture of chlorine and carbon monoxide it has been found possible to demonstrate that a small quantity of nitrosyl chloride not only—as with a mixture of chlorine and hydrogen—prevents almost entirely the combination of the gases under the influence of light, but, like oxygen and unlike nitrogen chloride exerts its influence without itself undergoing change. On the thermal union of chlorine and carbon monoxide the influence of nitrosyl chloride is inappreciable, a fact completely in agreement with the views that we hold on the nature of photochemical change. It was, in fact, mainly with the object of testing the latter consequence of our theory that the present investigation was undertaken.

#### EXPERIMENTAL.

In the preliminary experiments the actinometer was the same in construction as that used by Burgess and Chapman in the experiments on chlorine and hydrogen. The methods of controlling the temperature, of keeping the pressure at the open end of the index constant, and of adding measured volumes of foreign gases, were also the same as those adopted in previous investigations.

The chlorine was prepared from manganese dioxide and hydrochloric acid, and hydrogen chloride was removed from the gas by its being bubbled through previously boiled chlorine water. The manganese dioxide was digested for several hours with chlorine water, and the hydrochloric acid was made (with the precautions observed by Chapman and MacMahon) by dissolving hydrogen chloride (from pure sodium chloride and concentrated sulphuric acid) in dilute chlorine water which had been previously boiled for a long time in a large flask provided with a ground-in reflux condenser. The carbon monoxide was prepared from sodium formate and concentrated sulphuric acid, and was washed with potassium hydroxide solution. The mixture of equal volumes of chlorine and carbon monoxide was made (with special precautions to exclude air) in a glass gas-holder containing concentrated sulphuric acid which had been previously saturated with chlorine and boiled. In spite of all the precautions taken to destroy unstable inhibitive substances, the mixture of gases prepared by the above method exhibited a short "induction period" on exposure to light. This was not, however, a serious disadvantage in the preliminary experiments.

*The Inhibitive Influence of Nitric Oxide.*—The filling of the actinometer with the mixture of chlorine and carbon monoxide was accomplished by preliminary substitution of dry chlorine for the air in the insolation vessel, and subsequent displacement of the chlorine with a sensitive mixture of the gases. The actinometer

was illuminated with a 32 c.p. incandescent lamp placed at a distance of about 25 cm. from the insolation vessel. The distances in centimetres traversed by the boundary of the sulphuric acid in the index-tube in successive intervals of 2 minutes are recorded below.

Time in minutes.	Movements of index.
2	-0.70 cm.
4	1.80 "
6	3.20 "
8	3.40 "
10	3.40 "
12	3.20 "
14	3.40 "

It will be observed that there was a short induction period. 0.3 Per cent. by volume of nitric oxide was then introduced into the insolation vessel, which, after being left for a short time in the dark, was again exposed to the rays of the lamp. The index remained quite stationary, and even after a period of two days it had not moved. The shutters of the window in the darkened room were then thrown open. The window faces the north, and the sky at the time was rather dull. The daylight failed to bring about a noticeable combination of the gases. A carbon arc lamp fed with a current of ten amperes was then placed as close to the insolation vessel as the bath in which the latter was contained would permit. In this intense light a slow combination of the gases, corresponding with a movement of the index of 0.21 cm. in a minute, was observed. The insolation vessel was exposed to the arc lamp for different periods of time, amounting in all to twenty-four hours, and the rate of movement of the index meanwhile fell to 0.18 cm. per minute, the fall being obviously due to the gradually decreasing partial pressures of the chlorine and carbon monoxide. Nitroxy chloride is accordingly a very powerful inhibitor, and like oxygen is not removed from the system by the action of light.

*The Inhibitive Influence of Ozone and of Nitrogen Chloride:—* When mixtures of equal volumes of chlorine and carbon monoxide containing small quantities of ozone or nitrogen chloride were exposed to light, the occurrence of marked "induction periods" was observed. Ozone, being comparatively very unstable in the presence of chlorine, completely disappears from the mixture in a few hours. It was noticed that when nitrogen chloride was passed into the insolation vessel which contained the active mixture, a white deposit was formed on the inner surface of the glass. The character of this deposit has not yet been investigated. In its formation a considerable proportion of the nitrogen chloride must have been removed, and this would probably account for the fact that the observed "induction periods" were considerably shorter

than our knowledge of the effect of the same inhibitor on the union of chlorine and hydrogen had led us to expect.

*The Inhibitive Influence of Oxygen.*—The addition of even a small quantity of oxygen to an active mixture diminishes the sensitiveness considerably, but the fall in the sensitiveness effected by this means is not so great as that observed when a mixture in equivalent proportions of chlorine and hydrogen is subjected to the same treatment. It is possible that the sole cause of this difference is to be sought in the unequal degrees of freedom from initial contamination by oxygen of the respective mixtures. The electrolysis of concentrated hydrochloric acid, conducted with the precautions recommended by Bunsen and Roscoe, undoubtedly provides us with a means of preparing electrolytic gas contaminated with a smaller proportion of air than a mixture of chlorine and carbon monoxide, prepared by the method adopted in these experiments, contains.

It was owing to the circumstance that a mixture of chlorine and hydrogen can be obtained so free from inhibitive impurities that it was possible to show that the relation expressed by the equation:

$$[O] \times S = K$$

(in which  $[O]$  is the concentration of the oxygen,  $S$  is the sensitiveness, and  $K$  a constant) holds approximately for small concentrations of oxygen (Chapman and MacMahon, Trans., 1909, 95, 959). The same relation may be valid for a mixture of chlorine and carbon monoxide in equivalent proportions when the relative quantity of oxygen present in the mixture is small. The relation does not hold, however, when the oxygen is increased in amount. This will be made evident by an inspection of the following results furnished by the first experiment performed on this point.

#### Experiment I.

Oxygen introduced.	Sensitiveness.	$[O] \times S$ .
Original mixture .....	4.30	—
1.6 per cent. ....	1.60	2.56
4.8 „ „ .....	1.24	5.95

When the magnitude of  $[O]$  exceeds 1.5 per cent., the value of the product  $[O] \times S$  rises rapidly as the oxygen is further increased. From the above results it would appear to be probable that the sensitiveness approaches a limit as the percentage of oxygen is increased. To test this conjecture, the following experiment was performed. The actinometer was filled with a mixture of equal volumes of chlorine and carbon monoxide at a pressure of half an atmosphere. Oxygen was then admitted until its partial pressure was one quarter of an atmosphere, and, after the sensitive

ness had been measured, another equal quantity of oxygen was introduced, and the sensitiveness again taken. The results are recorded below.

*Experiment IIa.*

Oxygen introduced.	Sensitiveness.
25 per cent. ....	0.745
50 " " .....	0.733

Below are the results furnished by a second experiment performed in the same way.

*Experiment IIb.*

Oxygen introduced.	Sensitiveness.
25 per cent. ....	0.783
50 " " .....	0.738

In order to discover whether the value of the product  $[O] \times S$  approaches a limit as the amount of oxygen in the mixture is reduced, an experiment was performed in which the value of the sensitiveness of mixtures containing smaller amounts of oxygen was measured.

*Experiment III.*

Oxygen introduced.	Sensitiveness.	$[O] \times S$ .
0.44 per cent. ....	2.01	0.8844
0.88 " " .....	1.32	1.1616
1.76 " " .....	0.84	1.4784
3.52 " " .....	0.56	1.9712

A comparison of the results of all the experiments discloses a manifest tendency of the product  $[O] \times S$  to approach a limiting value as the amount of oxygen is reduced, and this tendency would be still more apparent if a correction were made for the small amount of oxygen contained in the original mixture. The values for the sensitiveness in the experiments I, II, and III are not comparable, since light of different intensities had to be employed in the separate experiments in order that the rates of combination might have the most convenient magnitudes.

It would appear that, as a first approximation, the sensitiveness of a mixture of chlorine and carbon monoxide in equivalent proportions containing oxygen at different partial pressures is given by the formula:

$$S = A + B/[O],$$

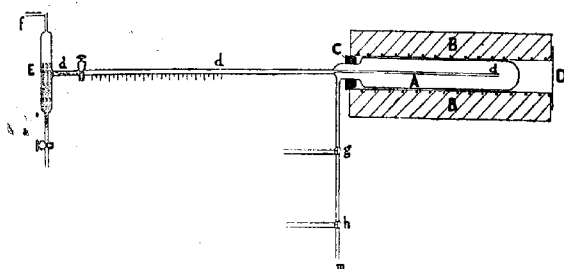
in which  $A$  and  $B$  are constants and  $S$  and  $[O]$  have the same significance as before. If  $[O]$  is small,  $S$  is so large that, in comparison,  $A$  becomes negligible; but if  $[O]$  is large,  $S$  becomes almost equal to  $A$ . That the sensitiveness of the mixture is independent of the partial pressure of the oxygen when the value of the latter is large, would seem to indicate that the effective energy is not homo-

geneous in character, and that in the degradation of certain forms of it, which constitute a small fraction of the whole, the oxygen plays a less important part than the other substances present in the mixture.

*Experiments at Higher Temperatures.*

The apparatus was designed so as to admit of the insolation vessel being heated and at the same time exposed to light. Fig. 1 is a diagrammatic representation of the actinometer. The insolation vessel *A* was enclosed in the porcelain tube of the electric resistance furnace *B*. One end of the porcelain tube was closed with the asbestos stopper *C*, and the other end with the transparent mica plate *D*, through which the light was admitted to the insolation vessel. The index tube *d* communicated with the reservoir *E*,

FIG. 1.



which contained sulphuric acid. The glass tube *f* at the top of *E* was connected to a large glass bottle, the air in which could be kept at any desired pressure. The current supplied to the furnace was regulated by an ammeter and an adjustable resistance. The gases were admitted to the insolation vessel through the tube *m*. As the actinometer could be partly or completely exhausted through the index tube *d*, and the pressure measured by a manometer connected with the large bottle mentioned above, but not shown in the figure, the filling with a mixture of known composition could be accomplished by admitting the gases separately to the insolation vessel. Before filling the actinometer, the air was driven out of it with a current of chlorine. The three-way taps *g* and *h* served the same purpose as formerly (Chapman and MacMahon, Trans., 1909, 95, 961).

For the earlier experiments a mixture of chlorine and carbon monoxide prepared as described above was used. It was found

that when the current heating the electric furnace was 2.35 amperes, corresponding with a temperature of  $350^{\circ}$ , the rate of union of the gases was conveniently rapid. We were surprised to find that the rates of interaction in the dark and in the light were almost the same at this temperature. The insolation vessel was alternately illuminated and shaded during intervals of time, each of four minutes' duration, and the position of the index at the end of every interval recorded. The mean rates of movement in the light and in the dark were:

Insolation vessel illuminated.  
6.58 cm. in 2 minutes.

Insolation vessel shaded.  
6.51 cm. in 2 minutes.

The source of illumination was an incandescent lamp of about 50 c.p. placed at a distance of 7 cm. from the mica window of the furnace.

In order to test if this unexpected result was due to the formation of some stable inhibitor at the high temperature, the insolation vessel was rapidly cooled immediately after the above measurements had been made, and the sensitiveness of the mixture taken at the ordinary temperature. The rate of movement of the index exceeded 8 cm. in two minutes, the illumination being the same as before. The cooling of the actinometer with sufficient rapidity to prevent further combination of the gases was accomplished by sliding the furnace to the right, and allowing the insolation vessel to cool in the open air.

The above experiment was repeated under the same conditions, with the exception that the incandescent lamp was displaced by a carbon arc, which was brought quite close to the mica window. The following measurements were obtained at the high temperature:

Insolation vessel illuminated.  
7.35 cm. in 2 minutes.

Insolation vessel shaded.  
6.56 cm. in 2 minutes.

The rate at which the gases in the insolation vessel combined after they had been cooled and then exposed to the same light was too rapid to admit of a measurement being made. The experiment was repeated several times, and always gave the same result. The mixture became insensitive to light at the higher temperature, and recovered its sensitiveness on being cooled. A short preliminary account of the phenomenon just described has been communicated (Proc., 1911, 27, 56), and it was therein stated that the experiments were being performed over a wider range of temperature. As the experiments in question have failed to elicit the information which we hoped to obtain from them, a brief general account of such of them as have furnished knowledge required in the subsequent investigation of other questions will suffice.

*The Photochemical Interaction of Chlorine and Carbon Monoxide  
at 170°.*

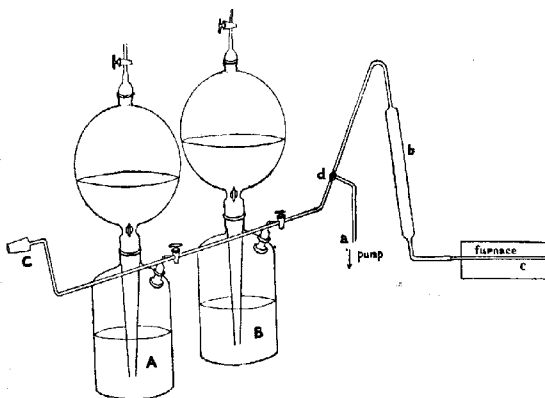
From the result of the foregoing experiment it might not unreasonably be expected that the temperature-coefficient of the rate of photochemical interaction of chlorine and carbon monoxide would be found to have a value less than unity. It is known that at the ordinary temperature photochemical changes, unlike spontaneous changes, are scarcely affected by a change of temperature of a few degrees. This was observed by Bunsen and Roscoe to be the case for the union of chlorine and hydrogen, and has since come to be regarded as the general rule. In order to obtain information on this interesting point, mixtures of chlorine and carbon monoxide were exposed successively to the same light at a temperature of 172° and at the ordinary temperature, and the rates of interaction compared. The results were, however, so irregular that attempts to find the influence of temperature on the rate of photochemical change had to be abandoned. Sometimes a mixture which at the ordinary temperature was very sensitive would, on exposure to light at the higher temperature, remain unchanged for an indefinite period of time, whereas, on other occasions, mixtures which were relatively insensitive at the lower temperature would prove to be only a little less sensitive at 172°. At length it became manifest that some impurity—an inhibitor the efficiency of which increases with the temperature—was affecting the results. Although we have endeavoured to identify the inhibitor in question, our efforts have been unavailing. We have, however, elaborated a process by which it is possible to prepare a mixture of chlorine and carbon monoxide sufficiently free from contamination with the objectionable impurity for the principal object we had in view. In this process oxygen is also almost completely eliminated, and the mixtures obtained are accordingly extremely sensitive. In Fig. 2 the essential parts of the apparatus used in the process are depicted.

The two gas-holders *A* and *B* contained water which had been thoroughly digested with chlorine, the use of sulphuric acid for confining the gases having been found to be unsatisfactory. The gas-holder *A* contained the carbon monoxide and the holder *B* the chlorine, the water in *B* having been, of course, saturated with the gas it was to contain. The ground-glass stopper *C* fitted into a long-necked flask, in which the gases were separately prepared. The air was removed from this flask by means of a pump connected to the tube *a*. The tube *b* was filled with fused calcium chloride. The further end of *b* communicated directly with a long quartz tube *c*,



surrounded by a furnace which could be raised to a temperature of about  $1000^{\circ}$ . The gases passed from *c* through a glass capillary tube into the insulation vessel. The whole apparatus between *d* (Fig. 2) and *h* (Fig. 1) could be exhausted through the tap *h*. After the gas-holders *A* and *B* had been filled with carbon monoxide and chlorine respectively, a small volume of chlorine was passed from *B* into *A*, and an equal volume of carbon monoxide from *A* into *B*. *A* then contained carbon monoxide mixed with about 1 per cent. of chlorine, and *B* contained chlorine mixed with the same percentage of carbon monoxide. The impurities capable of giving rise to an "induction period" were destroyed with the aid of the chlorine as the gases passed through the heated quartz tube *c*. At

FIG. 2.



the same time any oxygen present in the gases from either of the holders was almost entirely eliminated by its entering into combination with the carbon monoxide present.\* The gases were, of course, separately admitted to the actinometer. All the glass taps were lubricated with glacial phosphoric acid.†

\* At  $800^{\circ}$  and at atmospheric pressure, the dissociation of carbonyl chloride is approximately 90 per cent.; at  $1000^{\circ}$  it would be almost complete, whereas at the same temperature and pressure carbon dioxide is dissociated to the extent of only 0.004 per cent.

† The viscous fluid formed on the surface of a stick of glacial phosphoric acid, which has been exposed for a short time to the air and then kept in a dry atmosphere for some time, is a better lubricant for glass taps than phosphoric oxide which has been permitted to become moist. The lubricant formed from the oxide generally contains solid particles which, besides being in themselves a disadvantage,

## INTERACTION OF CHLORINE AND CARBON MONOXIDE. 1737.

It was found that if the mixture of chlorine and carbon monoxide was made from carbon monoxide which had been quite recently prepared, its sensitiveness to light fell rapidly as the temperature rose, whereas a mixture made from carbon monoxide which had been kept in the presence of water for several days was relatively much more sensitive at the higher temperatures. Under no conditions, however, have we ever been able to obtain a mixture which was not many times less sensitive above  $300^{\circ}$  than at the ordinary temperature.

### *The Influence of Nitric Oxide and of Oxygen on the Thermal and Photochemical Interaction of Chlorine and Carbon Monoxide.*

With chlorine and carbon monoxide prepared and treated in the manner described above, the following experiments were performed. The insolation vessel was filled with chlorine and heated for an hour at a temperature just below the softening point of glass. The actinometer was then exhausted, and the temperature of the furnace lowered to  $315^{\circ}$ . As soon as the temperature of the insolation vessel had become constant, chlorine was permitted to enter in a regular stream until the pressure had reached half an atmosphere. Carbon monoxide was then passed into the actinometer until the pressure was that of an atmosphere. The filling of the actinometer was accomplished in ten to fifteen minutes. Very shortly after the actinometer had been filled, the rate of movement of the index was recorded. It was 12.70 cm. in eight minutes, that is, 1.59 cm. per minute. An arc lamp was then placed at a distance of 25 cm. from the mica window of the furnace, and, with the insolation vessel exposed to, and shaded from, the light alternately for intervals of four minutes' duration, readings of the rate of movement of the index were taken. The means of the two series of readings were:

In the dark.	In the light.
1.66 cm. per minute	2.72 cm. per minute.

When the source of light was moved much closer to the mica window the rate of movement of the index increased to 5.65 cm. per minute. Incidentally, it may be mentioned that it is known from the results of other experiments that if the mixture had been rapidly cooled and then exposed to the same light at the ordinary temperature, the rate of movement of the index would have been too rapid to admit of a measurement being made. A small volume

facilitate the diffusion of atmospheric moisture into the space between the stopper and the barrel. A tap lubricated with glacial phosphoric acid will hold for weeks without the precaution being taken of protecting the lubricant from the action of the moisture of the air by an external coating of grease.

of nitric oxide was immediately admitted to the insolation vessel, and measurements of the rate of movement of the index in the light again made, the arc lamp being in its former position. The rate of movement of the index fell a little below that recorded for the thermal combination before the nitric oxide had been admitted, the actual value being 1.55 cm. per minute. The rate of movement of the index in the dark had precisely the same value. The presence of nitrosyl chloride therefore prevents the mixed gases from responding to light stimulus, but does not hinder their thermal interaction. The inhibitive effect of nitrosyl chloride is restricted to the photochemical change. The above experiment was repeated several times, the result being the same on every occasion.

It has been shown that, within the limits of accuracy attainable, oxygen is without catalytic influence on the pyrogenic union of chlorine and carbon monoxide. This was demonstrated by admitting oxygen to the actinometer whilst combination was proceeding, and observing that the rate of movement of the index did not alter. It is also evident that the effect of oxygen, if any, on the pyrogenic union of the gases must be negligible in comparison with its powerful influence on the photochemical change from the circumstance that the initial rate of pyrogenic union of chlorine and carbon monoxide has always practically the same value, at the same temperature, for mixtures of the gases in equal volumes, although the proportion of oxygen contained in mixtures prepared at different times must be very variable.

*The Homogeneity of the Thermal Interaction of Chlorine and Carbon Monoxide:*—In the study of spontaneous changes in gases, the first point to be ascertained before any conclusions of theoretical interest can be drawn is whether or not the observed change is mainly homogeneous. This point has accordingly been investigated in the present case, and, from the results of the experiments undertaken with this object in view, we conclude that the thermal union of chlorine and carbon monoxide under the conditions prevailing throughout this research may for all practical purposes be regarded as homogeneous in character. The experiments which establish this result are detailed below.

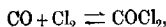
The insolation vessel of the actinometer was filled as rapidly as possible with a mixture of chlorine and carbon monoxide in the manner described above, and the rate of movement of the index during an interval of twenty minutes observed. The rate was 1.755 cm. per minute. The insolation vessel was then cooled, the furnace removed, and a hole fused in the end of the insolation vessel with the blow-pipe. Through this hole six grams of

thoroughly desiccated glass wool were introduced in such a manner as to fill the tube almost completely. The hole through which the glass wool had been introduced was then closed. The furnace was replaced, and the insulation vessel again raised to the temperature of  $345^{\circ}$ , dry chlorine being meanwhile slowly passed through it. The actinometer was then filled as before, and the initial rate of combination of the chlorine and carbon monoxide determined. The mean rate of movement of the index, taken as previously over a period of twenty minutes, was 2.226 cm. per minute. In order to compare this rate with that found when the actinometer contained no glass wool, an allowance must be made for the decreased volume of the gas. After making this correction, the following ratio was calculated:

$$\frac{\text{Rate with actinometer filled with glass wool}}{\text{Rate with actinometer empty}} = 1.237$$

The ratio of the surface of the glass in contact with the combining gases in the last experiment to that in the first experiment was estimated to be 23.3.

It is manifest from these numbers that glass is only a weak catalyst for the change:



and that in our experiments the thermal union of chlorine and carbon monoxide may for all practical purposes be regarded as a homogeneous change.

#### *General Conclusions.*

(1) In glass vessels the thermal interaction of chlorine and carbon monoxide is almost entirely homogeneous if the surface of the glass is not exceptionally large.

(2) The photochemical change is retarded, and in some cases almost entirely prevented from taking place, by small quantities of certain gases and vapours.

(3) The rate of the thermal change is not appreciably affected by the presence of small amounts of these inhibitors.

SIR LEOLINE JENKINS LABORATORIES,  
JERUS COLLEGE, OXFORD.

CXCV.—*The Reactivity of Ketones towards Iodine and the Relative Rates of Tautomeric Change. Part II.*

By HARRY MEDFORTH DAWSON and HARRY ARK, M.Sc.

IN continuation of previous experiments on the relative rates of tautomeric change of ketones (Dawson and Wheatley, *Trans.*, 1910, **97**, 2048) as measured by the velocity with which they react with iodine under the catalytic influence of a mineral acid, the authors have carried out a further series of measurements in which certain dialkyl ketones and substituted acetophenones were investigated.

As in the earlier series, the kinetic measurements were made at 25° in an aqueous-alcoholic solution containing 40 volumes per cent. of ethyl alcohol with 0.1 molar sulphuric acid as catalyst. When the ketone present in the solution is such that its concentration remains sensibly constant during the period in which the progress of the reaction is followed, the tautomeric change of the ketone proceeds, under normal conditions, with constant velocity, which is measured by the rate of disappearance of iodine added as indicator.

In pure aqueous solution it is necessary to add a small quantity of an iodide in order to bring the requisite amount of iodine into solution. Although the solubility of iodine in 40 per cent. alcohol is such that the addition of iodide is not absolutely necessary, the earlier measurements were, as a matter of fact, made with solutions which contained small quantities of potassium iodide in order to diminish errors resulting from the volatility of the free iodine. For many ketones the reaction proceeds in exactly the same way and at the same rate, whether potassium iodide is present or not, but this is not always the case.

In the estimation of the enolised ketone a measured volume of the solution was added to a slight excess of sodium acetate in order to destroy the catalytic action of the mineral acid, and the resulting solution was then titrated with a freshly prepared 0.1*N*-sodium thio-sulphate solution. In the case of methyl isopropyl ketone and pinacolin, it was observed that the end-point was very ill-defined, and that the blue colour of the starch-paste returned very quickly. This pointed to the liberation of iodine from the iodide present in the solution, and blank tests, in which the ketones were added to an acidified solution of potassium iodide, showed that iodine was liberated in considerable quantity and at a rapid rate. Liberation of iodine from the iodide was also observed with benzyl methyl

ketone, dibenzyl ketone, deoxybenzoin, and methyl isobutyl ketone, although the quantity set free and the speed of the reaction were much smaller than in the case of methyl isopropyl ketone and pinacolin.

The nature of this disturbing reaction has not been more closely examined, and it is not yet known whether it is of the same kind in all cases. It seems probable that the liberation of iodine in solutions of dibenzyl ketone is connected with the oxidation of this substance by atmospheric oxygen (Forley, *Trans.*, 1899, **75**, 871), whereby phenylacetic acid and benzaldehyde are produced. In consequence of the further oxidation of the aldehyde, iodine will then be set free from the iodide (compare Baeyer and Villiger, *Ber.*, 1900, **33**, 1569).

In consequence of this liberation of iodine from iodides by certain ketones, it was necessary, in such cases, to eliminate the iodide from the solutions employed in the dynamic measurements. This reduces the disturbing effect to a very large extent, but does not entirely eliminate it, for, as the iodine disappears by combination with the enolised ketone, it is replaced by an equimolecular quantity of hydrogen iodide, from which iodine will be again set free to some extent by the action of the ketone. The concentration of the hydrogen iodide is, however, so small, even when the reaction is completed, that the quantity of iodine thus liberated is not such as to prevent the determination of the rate of tautomeric change. There can be little doubt, however, that the subsequent liberation of iodine from the hydrogen iodide formed during the reaction is responsible for the slight decrease in the reaction velocity which was observed in certain cases towards the end of the period of observation.

For a given concentration of the acid catalyst the rate of change is proportional to the concentration of the ketone, and table I gives a summary of the velocities of tautomeric change ( $k$ ) referred to a ketone concentration of one mol. per litre and 0.1 molar sulphuric acid as catalyst. In the majority of the experiments the actual concentration of the ketone varied from 0.12 to 0.18 mol. per litre, and the added iodine corresponded with an original concentration of about 0.01 mol. per litre. To permit of a direct comparison of the rates of enolisation of closely related ketones, some of the data obtained in the previous series of measurements have been expressed in terms of unit ketone concentration and incorporated in the table.

TABLE I.

	$k \times 10^4$		$k \times 10^4$
Dimethyl ketone .....	288	Methyl butyl ketone.....	318
Diethyl ketone .....	286	Methyl isobutyl ketone.....	247
Dipropyl ketone.....	202	Methyl <i>tert.</i> -butyl ketone...	132
Methyl propyl ketone .....	270	Methyl hexyl ketone.....	306
Methyl isopropyl ketone ...	200	Acetophenone .....	108
		Benzyl methyl ketone .....	395
		Propiophenone .....	24

From the above data it is evident that the rate of tautomeric change of symmetrical aliphatic ketones diminishes as the number of carbon atoms in the alkyl group increases. The percentage decrease in the reactivity is approximately the same on passing from the dimethyl to the diethyl ketones as in the transition from the diethyl to the dipropyl compound. In contrast with this regularity it should be noted that the reactivities of the successive methyl alkyl ketones vary irregularly, as is evident from the series—dimethyl (288), methyl ethyl (300), methyl propyl (270), methyl butyl (318), methyl hexyl (306). It does not seem possible at present to offer any satisfactory explanation of the observed differences.

The influence of the constitution of the alkyl group in this series is, however, clearly defined, as is seen by a comparison of the two methyl propyl and the three methyl butyl ketones. Substitution of the normal by the *iso*alkyl group reduces the reactivity in each case by about 25 per cent., whilst the reactivity of the normal butyl ketone is about two and a-half times as great as that of the corresponding tertiary butyl compound. These changes in reactivity are in the direction anticipated, for the replacement of one of the two reactive hydrogen atoms in the normal alkyl group must lead to a diminution in the reactivity of the ketone if the alkyl group in question is directly concerned in the tautomeric change. In the case of methyl *tert.*-butyl ketone, the butyl group represents an inactive radicle, and the methyl group alone can be involved in the tautomeric change. Compared with dimethyl ketone, it may be noticed that the reactivity of methyl *tert.*-butyl ketone is approximately one half as large, a relationship which may serve to throw some light on the nature of the keto  $\rightarrow$  enol transformation in the case of the dialkyl ketones. On the other hand, the reactivity of acetophenone, which also contains a non-reactive group, is considerably smaller than that of methyl *tert.*-butyl ketone, which shows that the tendency of the  $\text{CH}_3\cdot\text{CO}\cdot$  group to undergo enolisation is appreciably diminished by the proximity of the negative phenyl group. It is evident, however, that the part played by the

phenyl group. Its influence on the interaction between alkyl hydrogen and the ketonic group is of a somewhat complex character, for the rate of tautomeric change of benzyl methyl ketone is greater than that of any other ketone which has been investigated. In the expectation that dibenzyl ketone would exhibit a still greater rate of change, experiments were also made with this substance. This supposition was not confirmed, but since the rate of progress of the change, as measured by the fall in the iodine concentration, is not constant, it is probable that some other change is involved, and, in consequence, a quantitative comparison of this substance with other ketones is out of the question.

In table II are recorded the rates of tautomeric change of certain substituted acetophenones. These measurements were undertaken in order to ascertain the influence of substitution in the benzene nucleus on the enolisation tendency of the  $\text{CH}_3\text{CO}$  group. On account of the smaller solubility of these ketones in 40 per cent. alcohol, it was necessary to conduct the investigation of these in more dilute solution. The concentration of the ketone was about 0.025 molar, that of the iodine initially present about 0.004 molar, with 0.1 molar sulphuric acid as catalyst. Parallel experiments with and without potassium iodide gave practically identical results, and blank experiments, in which the catalysing acid was absent, showed only relatively small changes in the iodine titre during the time occupied by the observations with the acid catalyst, except in the case of *p*-aminoacetophenone. In the blank experiment with this, a quantity of sulphuric acid equivalent to the ketone present was added, and the rate of disappearance of iodine observed under these conditions was applied to the correction of the data obtained when the acid added was in excess of that of the ketone to the extent of 0.1 mol. per litre.

TABLE II.

Ketone.	$k \times 10^4$ .
Acetophenone .....	108
<i>p</i> -Bromoacetophenone .....	90
<i>p</i> -Iodoacetophenone .....	(90)*
<i>p</i> -Aminoacetophenone sulphate .....	80
<i>m</i> -Nitroacetophenone .....	45
<i>o</i> -Bromoacetophenone .....	0

According to these data, substitution of hydrogen in the phenyl group by bromine, iodine, the nitro-group, or the acidified amino-group leads to a reduction of the rate of tautomeric change. If

\* On account of the small solubility of this substance it was examined in 60 per cent. alcoholic solution and found to change at the same rate as the corresponding bromo-compound.



the positive character of the amino-group is more than neutralised by the mineral acid, the effect of the substituent is in all cases to increase the negative character of the phenyl group, and this is doubtless the cause of the diminished rate of enolisation.

In the case of  $\omega$ -bromoacetophenone, the change, if it occurs at all, takes place very slowly, and the substitution of a hydrogen atom of the methyl group by a negative atom or group would therefore appear to inhibit the tautomeric change.

#### EXPERIMENTAL.

In the appended tables some of the dynamic measurements are recorded, from which the relative reactivities of the ketones have been calculated. In these tables  $c$  represents the ketone concentration,  $x$  the observed iodine concentration at time  $t$ ,  $x_0$  the concentration at  $t=0$ , and  $x_t$  the concentration calculated from  $x_t = x_0 - kt$ , in which  $k'$  is the constant rate of change. Concentrations are expressed in mols. per litre, time in minutes.

##### *Dipropyl Ketone.*

$$c = 0.1532; k' = 31.0 \times 10^{-6}.$$

$t$	0.	30.	60.	90.	130.
$x.10^4$	90.7	81.4	72.4	62.8	50.9
$x_t.10^4$	(90.7)	81.4	72.1	62.8	50.4

##### *Methyl isoPropyl Ketone.*

$$c = 0.185; k' = 36.5 \times 10^{-6}.$$

$t$	0.	20.	40.	70.	100.	130.
$x.10^4$	91.9	84.7	77.2	66.2	55.5	45.1
$x_t.10^4$	(91.9)	84.6	77.3	66.4	55.4	44.5

##### *Methyl isoButyl Ketone.*

$$c = 0.1512; k' = 37.3 \times 10^{-6}.$$

$t$	0.	30.	60.	90.	120.
$x.10^4$	101.3	90.1	79.0	68.2	58.2
$x_t.10^4$	(101.3)	90.1	78.9	67.7	56.6

##### *Methyl tert.-Butyl Ketone.*

$$c = 0.1285; k' = 17.0 \times 10^{-6}.$$

$t$	0.	40.	100.	140.	180.	220.
$x.10^4$	88.6	81.2	71.2	64.8	58.4	51.9
$x_t.10^4$	(88.6)	81.8	71.6	64.8	58.0	51.2

*Benzyl Methyl Ketone.*

$$c=0.121; k'=48.0 \times 10^{-6}.$$

<i>t.</i>	0.	40.	60.	85.	105.
$x.10^4$	77.5	57.1	48.4	36.4	27.4
$x_0.10^4$	(77.5)	58.3	48.7	36.7	27.1

*Acetophenone.*

$$c=0.0274; k'=2.95 \times 10^{-6}.$$

<i>t.</i>	0.	150.	257.	347.	430.
$x.10^4$	38.8	34.5	31.3	28.6	26.0
$x_0.10^4$	(38.8)	34.4	31.2	28.6	26.1

*p-Bromoacetophenone.*

$$c=0.0250; k'=2.2 \times 10^{-6}.$$

<i>t.</i>	0.	120.	240.	360.
$x.10^4$	40.1	37.5	34.8	32.1
$x_0.10^4$	(40.1)	37.45	34.8	32.2

*m-Nitroacetophenone.*

$$c=0.0251; k'=1.1 \times 10^{-6}.$$

<i>t.</i>	0.	120.	240.	360.
$x.10^4$	40.0	38.7	37.4	36.1
$x_0.10^4$	(40.0)	38.7	37.35	36.05

*p-Aminoacetophenone Sulphate.*

$$c=0.0247; k'=1.95 \times 10^{-6}.$$

<i>t.</i>	0.	60.	230.	320.	443.
$x.10^4$	37.95	36.4	33.7	31.7	29.35*
$x_0.10^4$	(37.95)	36.6	33.45	31.7	29.3

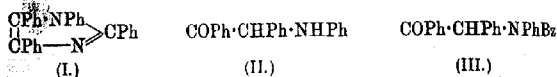
PHYSICAL CHEMISTRY LABORATORY,  
THE UNIVERSITY, LEEDS.

\* These numbers are corrected for the rate at which iodine was found to disappear in a parallel experiment without acid catalyst.

**OXCVI.—The Formation of Glyoxalines from Acyl Derivatives of  $\alpha$ -Keto- $\beta$ -anilino- $\alpha\beta$ -diphenylethane.**

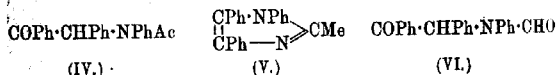
By ARTHUR ERNEST EVEREST (Priestley Research Scholar of the University of Birmingham) and HAMILTON MCCOMBE.

IN the course of some work in these laboratories on the action of heat on a mixture of benzaldehydecyanohydrin and aniline, a compound was isolated, which, on analysis, was found to have the empirical formula  $C_{27}H_{29}N_2$ . This substance was found to be basic, readily yielding well-characterised, stable salts, and it could be distilled without decomposition. It was suspected that this compound was 1:2:4:5-tetraphenylglyoxaline (I), and, as  $\alpha$ -keto- $\beta$ -anilino- $\alpha\beta$ -diphenylethane (II) was also one of the products isolated in this reaction, an attempt was made to synthesise the tetraphenylglyoxaline with  $\alpha$ -keto- $\beta$ -anilino- $\alpha\beta$ -diphenylethane as the starting point. This synthesis proved successful:

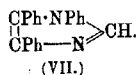


The first step in the synthesis consisted in the conversion of  $\alpha$ -keto- $\beta$ -anilino- $\alpha\beta$ -diphenylethane into  $\alpha$ -keto- $\beta$ -benzoylanilino- $\alpha\beta$ -diphenylethane (III). This benzoyl derivative was then heated in a sealed tube with aqueous ammonia, and the tetraphenylglyoxaline thus obtained.

An attempt was next made to bring about a similar condensation to glyoxalines employing other acyl derivatives of  $\alpha$ -keto- $\beta$ -anilino- $\alpha\beta$ -diphenylethane. The acetyl derivative (IV), when heated in a sealed tube with aqueous ammonia, was found to yield 1:4:5-triphenyl-2-methylglyoxaline (V):

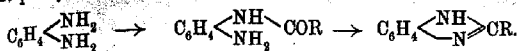


In a similar manner, the formyl derivative of  $\alpha$ -keto- $\beta$ -anilino- $\alpha\beta$ -diphenylethane (VI) yielded 1:4:5-triphenylglyoxaline (VII):



This method for the preparation of glyoxalines is similar to Ladenburg's method for the formation of benziminazoles (*Ber.*, 1875, 8, 677; 1878, 11, 826) by the condensation of *o*-phenylene-

diamines with an acid chloride or anhydride; acyl compounds of the phenylenediamine are formed as intermediate products; thus:



Another series of somewhat similar reactions has been described by Meldola and Hay (Trans., 1908, **93**, 1695; 1909, **95**, 1033), where these investigators describe the formation of benziminazoles by the interaction of 2:3:5-trinitro-4-acetylaminophenol with primary amines.

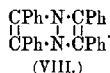
By means of the reaction which we describe in this communication, we are furnished with a ready means of obtaining glyoxalines with substituents attached to the nitrogen atom. Previously, such substituted glyoxalines could be obtained by two methods, neither of which is very convenient.

(1) By treating the silver salt of the glyoxaline with an alkyl iodide. This method has the great disadvantage that the substituent introduced must be an aliphatic radicle.

(2) By oxidation of the mercaptans of the glyoxalines which are obtained from the thiocarbamides (Ber., 1889, **22**, 1353; 1892, **25**, 2354; 1893, **26**, 2204).

This reaction consists in closing up a chain of four atoms to a ring consisting of five atoms, and thus gives us a closer insight than has been previously possible into the actual mechanism of the ordinary glyoxaline formation from  $\alpha$ -diketones, ammonia, and an aldehyde.

In the formation of these three glyoxalines by heating together the acyl derivatives of  $\alpha$ -keto- $\beta$ -anilino- $\alpha\beta$ -diphenylethane with ammonia, there was obtained, in varying quantities, a second substance, which analyses showed to have the composition  $\text{C}_{28}\text{H}_{20}\text{N}_2$ . This substance is 2:3:5:6-tetraphenylpyrazine (VIII):

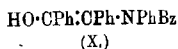
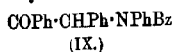


2:3:5:6-Tetraphenylpyrazine has been obtained in different ways by several investigators. Bülow (Ber., 1893, **26**, 1973) prepared it by boiling together benzaldehyde and formamide for two hours. It has also been obtained by J. Erdmann (Annalen, 1865, **135**, 55), Japp and Wilson (Trans., 1886, **49**, 826), and Leucart (J. pr. Chem., 1890, [ii], **41**, 333) by heating benzoin with alcoholic ammonia. It is doubtless by means of the latter reaction that the substance is formed in the present case, hydrolysis of the acyl- $\alpha$ -keto- $\beta$ -anilino- $\alpha\beta$ -diphenylethane to benzoin preceding that reaction.

Some interesting and characteristic colour changes are noticeable

in dealing with  $\alpha$ -keto- $\beta$ -anilino- $\alpha\beta$ -diphenylethane and its acyl derivatives in acid and in alkaline solutions.

$\alpha$ -Keto- $\beta$ -anilino- $\alpha\beta$ -diphenylethane itself is yellow, and gives rise to yellow solutions, but these solutions become colourless on the addition of acids, whilst the yellow colour is restored on the addition of alkali. The acyl derivatives are all white solids giving colourless solutions, but these solutions become deep yellow on the addition of a drop of alkali, and the colour is destroyed by the addition of acid. These colour changes seem to indicate the existence of each of these substances in two modifications; most probably these two are the ketonic and the enolic modifications. Thus, for the benzoyl derivative itself, the free substance most probably has the ketonic structure represented by the formula IX, whilst in the presence of alkali it has the enolic structure represented by the formula X. It is hoped to investigate this change more fully at a later date:



#### EXPERIMENTAL.

##### *$\alpha$ -Keto- $\beta$ -benzoylanilino- $\alpha\beta$ -diphenylethane* (III, p. 1746).

This substance was prepared from  $\alpha$ -keto- $\beta$ -anilino- $\alpha\beta$ -diphenylethane by the Schotten-Baumann reaction. When crystallised from methylated spirit or methyl alcohol, it separates in shining, colourless plates or leaflets, melting at  $149^{\circ}$ . Its alcoholic solution gives a yellow coloration on the addition of alkali, but this coloration is destroyed by neutralising the solution with acid:

0.2196 gave 0.6676  $\text{CO}_2$  and 0.1084  $\text{H}_2\text{O}$ .  $\text{C} = 82.91$ ;  $\text{H} = 5.48$ .  
 $\text{C}_{27}\text{H}_{21}\text{O}_2\text{N}$  requires  $\text{C} = 82.87$ ;  $\text{H} = 5.37$  per cent.

##### *1:2:4:5-Tetraphenylglyoxaline*, $\text{C}_{27}\text{H}_{20}\text{N}_2$ (I, p. 1746).

This substance was obtained by heating equal parts by weight of concentrated aqueous ammonia (D 0.880) and the above compound in a sealed tube to  $210$ – $220^{\circ}$  for seven or eight hours. The product, a sticky, yellow, crystalline mass, was washed free from resins with a small quantity of ether, then crystallised from methylated spirit. A yield of about 70–80 per cent. was obtained.

*1:2:4:5-Tetraphenylglyoxaline* separates from alcohol in long, colourless needles, melting at  $215^{\circ}$ . It is readily soluble in glacial acetic acid, aniline, or benzene, fairly so in hot absolute alcohol, methyl alcohol, acetone, or light petroleum, but less so in the cold solvents, and crystallises well from any of them; it is very sparingly

DERIVATIVES OF  $\alpha$ -KETO- $\beta$ -ANILINO- $\alpha\beta$ -DIPHENYLETHANE. 1749

soluble in ether; and is insoluble in water. It is stable towards alkalis, and can be distilled unchanged:

0.1819 gave 0.5793  $\text{CO}_2$  and 0.0917  $\text{H}_2\text{O}$ .  $\text{C}=87.06$ ;  $\text{H}=5.60$ .

0.1884 „ 12.70 c.c.  $\text{N}_2$  at  $20^\circ$  and 730.2 mm.  $\text{N}=7.54$ .

M.W. (by platinum salt) = 376.5, 366.0, 374.5.

$\text{C}_{27}\text{H}_{20}\text{N}_2$  requires  $\text{C}=87.10$ ;  $\text{H}=5.38$ ;  $\text{N}=7.53$  per cent.

M.W. = 372.

In addition to the above-described glyoxaline, a substance, crystallising in fine, needle-shaped crystals, and melting at  $243^\circ$ , was always encountered when crystallising the crude product for the first time. This substance remained as an almost totally insoluble residue when the glyoxaline was dissolved in boiling methylated spirit. The quantity of this substance formed was small, only constituting about 1—2 per cent. of the weight of the glyoxaline. It was recrystallised from amyl alcohol, and proved to be 2:3:5:6-tetraphenylpyrazine (VIII). There separated also from the mother liquors from which the glyoxaline had been recrystallised, a very small quantity of a substance melting at  $193$ — $195^\circ$ ; sufficient of this substance for further examination was not obtained.

1:2:4:5-Tetraphenylglyoxaline picrate,  $\text{C}_{27}\text{H}_{20}\text{N}_2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , was prepared by adding a concentrated solution of picric acid in glacial acetic acid to a solution of the glyoxaline in the same solvent at about  $100^\circ$ . The colour deepened very considerably on mixing, and, on cooling, golden-yellow, shining leaflets separated. The picrate may be recrystallised from glacial acetic acid, or, better, from methylated spirit. It melts at  $199^\circ$ :

0.2510 gave 0.6039  $\text{CO}_2$  and 0.0910  $\text{H}_2\text{O}$ .  $\text{C}=65.62$ ;  $\text{H}=3.99$ .

$\text{C}_{33}\text{H}_{23}\text{O}_7\text{N}_5$  requires  $\text{C}=65.89$ ;  $\text{H}=3.83$  per cent.

The hydrochloride, after recrystallisation from glacial acetic acid, separates in large, transparent cubes, melting at  $250^\circ$ .

The platinichloride forms a salmon-pink, microscopically crystalline precipitate:

0.4045 gave 0.0680 Pt. Pt = 16.81.

$(\text{C}_{27}\text{H}_{20}\text{N}_2)_2\text{H}_2\text{PtCl}_6$  requires Pt = 16.88 per cent.

$\alpha$ -Keto- $\beta$ -acetylanilino- $\alpha\beta$ -diphenylethane (IV, p. 1746).

This compound was prepared by Voigt (*J. pr. Chem.*, 1886, [ii], 34, 9), but the method described by this investigator, using acetic anhydride alone, did not give a very satisfactory product, so that it was modified to the following: 17 grams of the base, 15 grams of acetic anhydride, and 2 grams of acetyl chloride were heated for a few minutes on a water-bath, and the product was poured

into cold water. The reaction was found to proceed smoothly only when some acetyl chloride was used in addition to the acetic anhydride. The product crystallised from ethyl or methyl alcohol in slender, colourless, glistening scales (or leaflets), melting at 153°.

This substance, like the benzoyl derivative, gave a deep yellow coloration when potassium hydroxide was added to an alcoholic solution; this colour disappeared with excess of acid.

1:4:5-Triphenyl-2-methylglyoxaline,  $C_{22}H_{18}N_2$  (V, p. 1746).

This compound was prepared by heating equal parts by weight of aqueous ammonia (D 0.880) and the substance just described in a sealed tube to 200–230° for six to eight hours. On cooling the product, which resembled that from the benzoyl derivative, was washed with a small quantity of ether, and recrystallised from methyl alcohol, when the glyoxaline separated in fairly large, colourless crystals, melting at 194°. The yield was 70–90 per cent. of the theoretical. A small quantity of tetraphenylpyrazine was also obtained:

0.2196 gave 0.6841  $CO_2$  and 0.1172  $H_2O$ .  $C=84.93$ ;  $H=6.07$ .

0.1778 „ 13.40 c.c.  $N_2$  at 9.0° and 743.9 mm.  $N=8.93$ .

$C_{22}H_{18}N_2$  requires  $C=85.16$ ;  $H=5.81$ ;  $N=9.03$  per cent.

The *picrate* crystallises from methylated spirit in golden-yellow needles, melting at 180°:

0.2011 gave 0.4577  $CO_2$  and 0.0724  $H_2O$ .  $C=62.11$ ;  $H=4.02$ .

$C_{22}H_{18}N_2 \cdot C_6H_5O_7N_3$  requires  $C=62.34$ ;  $H=3.90$  per cent.

The *hydrochloride* separates from amyl alcohol in small, colourless crystals, melting sharply at 300°, with decomposition and evolution of gas.

The *platimchloride* was obtained as a salmon-pink, crystalline powder. It was best prepared from cold solutions, as the product was prone to accumulate in great masses if the reaction was carried out in hot solutions:

0.4420 gave 0.0830 Pt. Pt=18.78.

$(C_{22}H_{18}N_2)_2 \cdot H_2PtCl_6$  requires Pt=18.93 per cent.

$\alpha$ -Keto- $\beta$ -formylanilino- $\alpha\beta$ -diphenylethane (VI, p. 1746).

This substance was prepared by heating a mixture of two parts of the pure base with one part of anhydrous formic acid under reflux for about an hour. The resulting mixture was poured into cold water, when a semi-solid paste was obtained. Most of the excess of acid was then neutralised by sodium carbonate, after which the paste was sufficiently firm to allow of pouring off the water. After this had been done, the paste was dissolved in more than enough methylated spirit to keep all in solution in the cold,

and the excess of formic acid that still remained was neutralised by adding potassium hydroxide drop by drop until the colour of the solution turned to a deep yellow; after this process had been completed the whole of the product should still be in solution.

The alcoholic solution was then allowed to evaporate slowly in the cold, when the formyl derivative separated in colourless scales. The product thus obtained was recrystallised many times from methyl alcohol, and finally separated in small, colourless crystals, melting at  $105^{\circ}$ . This derivative was very soluble in most solvents. Like the benzoyl and acetyl derivatives it gave a deep yellow coloration with potassium hydroxide, which was destroyed on neutralising the solution with acid:

0.2511 gave 0.7338  $\text{CO}_2$  and 0.1251  $\text{H}_2\text{O}$ .  $\text{C}=79.70$ ;  $\text{H}=5.54$ .  
 $\text{C}_{21}\text{H}_{19}\text{O}_2\text{N}$  requires  $\text{C}=80.00$ ;  $\text{H}=5.40$  per cent.

1:4:5-Triphenylglyoxaline,  $\text{C}_{21}\text{H}_{16}\text{N}_2$  (VII, p. 1746).

This substance was prepared by heating together in a sealed tube for six to eight hours at  $210$ – $220^{\circ}$  equal quantities by weight of the formyl derivative just described and aqueous ammonia. The product resembled that obtained in the other cases, and was treated in the same manner. The glyoxaline was finally recrystallised from a mixture of three parts of methyl alcohol to two parts of water (by volume); from this mixture it separated in fine, silky needles, melting at  $172^{\circ}$ . The crystals were colourless, and very soluble in most solvents. The glyoxaline could be distilled unchanged. A small quantity of tetraphenylpyrazine was also formed:

0.1547 gave 0.4810  $\text{CO}_2$  and 0.0781  $\text{H}_2\text{O}$ .  $\text{C}=84.80$ ;  $\text{H}=5.61$ .  
 $\text{C}_{21}\text{H}_{16}\text{N}_2$  requires  $\text{C}=85.14$ ;  $\text{H}=5.41$  per cent.

The *picrate* crystallises from methyl alcohol in golden-yellow, needle-shaped crystals, melting at  $215^{\circ}$ :

0.1743 gave 0.3871  $\text{CO}_2$  and 0.0603  $\text{H}_2\text{O}$ .  $\text{C}=62.13$ ;  $\text{H}=3.84$ .  
 $\text{C}_{21}\text{H}_{16}\text{N}_2 \cdot \text{C}_6\text{H}_3\text{N}_3\text{O}_7$  requires  $\text{C}=61.72$ ;  $\text{H}=3.62$  per cent.

The *hydrochloride*, as it proved to be very soluble in most solvents, was not isolated, but the *platinichloride* was prepared, and crystallised from dilute acetic acid:

0.0914 gave 0.0178 Pt.  $\text{Pt}=19.47$ .  
 $(\text{C}_{21}\text{H}_{16}\text{N}_2)_2 \cdot \text{H}_2\text{PtCl}_6$  requires  $\text{Pt}=19.46$  per cent.

It is intended to extend this method to the synthesis of other glyoxalines and similar compounds.



CXCVII. — *The Effect of Heat on a Mixture of Benzaldehydecyanohydrin and Aniline.*

By ARTHUR ERNEST EVEREST (Priestley Research Scholar of the University of Birmingham) and HAMILTON MCCOMBIE.

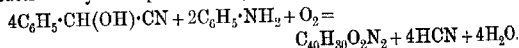
SOME years ago, in the course of some work in these laboratories, it was observed that if benzylideneaniline and benzaldehydecyanohydrin are heated together for forty-eight to ninety-six hours, a white, crystalline substance with an exceptionally high melting point (above  $350^{\circ}$ ) separated out from the boiling liquid. As the reaction took a long time to reach completion, it was probable that the benzylideneaniline was decomposed into its generators. Accordingly, a study was made of the products formed by the action of heat on a mixture of aniline and benzaldehydecyanohydrin.

When molecular proportions of these substances are heated together to  $150^{\circ}$ , before the end of half an hour a considerable amount of water is formed, and after that period the quantity of water does not increase. On cooling the product at this stage, anilinophenylacetoneitrile may be isolated.

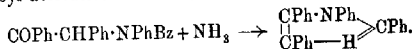
On heating the mixture of aniline and cyanohydrin for forty-eight to ninety-six hours, the following products were obtained:

- (1) Dibenzoyldianilinostilbene,  $\text{NPhBz} \cdot \text{CPh} : \text{CPh} \cdot \text{NPhBz}$ .
- (2) 1:2:4:5-Tetraphenylglyoxaline (Everest and McCombie, this vol., p. 1748).
- (3)  $\alpha$ -Keto- $\beta$ -anilino- $\alpha\beta$ -diphenylethane.
- (4) Benzanilide.

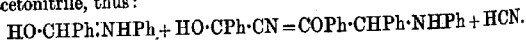
In the formation of compound (1) oxidation by the atmospheric oxygen must be assumed, and hydrocyanic acid is evolved. The reaction may be represented by the following equation:



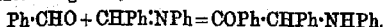
The formation of substance (2) must be due to the action of ammonia (formed by the hydrolysis of the hydrocyanic acid) on the benzoyl derivative of  $\alpha$ -keto- $\beta$ -anilino- $\alpha\beta$ -diphenylethane:



The formation of compound (3) in this reaction may be explained in three ways. The benzaldehyde may condense to benzoin, and this may undergo further condensation with aniline, or hydrocyanic acid may be eliminated from the cyanohydrin and phenylanilinoacetoneitrile, thus:

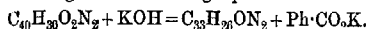


The third alternative is that benzaldehyde and benzyldianiline might condense together, thus:



The last method of formation is similar to the preparation of  $\alpha$ -keto- $\beta$ -*p*-toluidino- $\alpha\beta$ -diphenylethane from benzyldiene-*p*-toluidine and benzaldehyde by the action of potassium cyanide (*Ber.*, 1896, 29, 1736).

The constitution of dibenzoyldianilinostilbene is established as follows: the analytical figures are in agreement with the formula  $\text{C}_{40}\text{H}_{30}\text{O}_2\text{N}_2$ , and it can be decomposed quantitatively by potassium hydroxide according to the following equation:

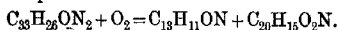


The substance formed in this reaction is benzyldianilinostilbene, and its constitution is shown by its decompositions, which take place in two ways:

(a) by spontaneous oxidation of its solutions when exposed to the air;

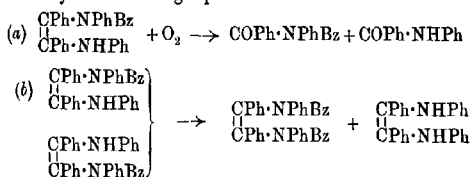
(b) by heating the substance to 120–140°.

In the former case, solutions of the substance in several solvents underwent decomposition into benzanilide and dibenzoylaniline:



In the latter case, heat decomposed the substance, so that dibenzoyldianilinostilbene was regenerated, and benzanilide and benzildianil were produced.

The decompositions of benzyldianilinostilbene are readily explained by the following equations:

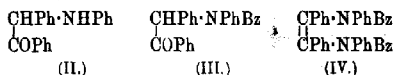


(L)

Dianilinostilbene (I), which one would expect to be formed in this reaction, is oxidised by the oxygen of the air, forming benzanilide, or it may undergo a simultaneous rearrangement and oxidation, resulting in the production of benzildianil,  $\text{NPh}\cdot\text{CPh}\cdot\text{CPh}\cdot\text{NPh}$ . Both these products have been identified in the reaction mixture.

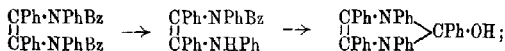
If these conclusions be correct, then it should not be a matter of great difficulty to synthesise dibenzoyldianilinostilbene in such a way that its constitution would be obvious. A successful attempt was made by taking advantage of the above-mentioned decomposi-

tion by heat of monobenzoyldianilinosilbene.  $\alpha$ -Keto- $\beta$ -anilino- $\alpha\beta$ -diphenylethane (II) was used as the starting point, and this was converted into the benzoyl derivative (III), which was then heated with aniline in the presence of potassium cyanide, when dibenzoyldianilinosilbene was obtained:

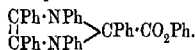


The occurrence of  $\alpha$ -keto- $\beta$ -anilino- $\alpha\beta$ -diphenylethane and benzamide in the tars formed in the reaction under investigation is in keeping with the above conclusions, and the course of the original reaction may, in all probability, be represented thus: benzaldehyde, in presence of hydrocyanic acid, undergoes condensation to benzoin, and this combining with the aniline present gives rise to the production of  $\alpha$ -keto- $\beta$ -anilino- $\alpha\beta$ -diphenylethane. The next step consists in the benzoylation of the latter compound by the benzaldehyde in the presence of the atmospheric air, and then the benzoyl derivative thus produced condenses with aniline to yield monobenzoyldianilinosilbene, which is then decomposed, with the production of dibenzoyldianilinosilbene.

The reason that only one benzoyl group is eliminated by potassium hydroxide from dibenzoyldianilinosilbene may be that ring formation takes place. One benzoyl group might be eliminated from dibenzoyldianilinosilbene and a cyclic compound formed, thus:



or, again, it is possible that the substance of high melting point may itself be a cyclic compound:



If, however, we assume these ring formulae, we should have great difficulty in explaining the ready decompositions of the yellow base, both in solution and in the free state.

All attempts to obtain salts from dibenzoyldianilinosilbene resulted in the elimination of benzoic acid and the formation of the same salts as were obtainable from the monobenzoyl derivative. The only true derivative of the dibenzoyl compound which could be prepared was its compound with methyl iodide.

Benzoyldianilinosilbene yields a series of salts, of which the hydrochloride, platinichloride, and acetate were obtained. On attempting to prepare a picrate from either the dibenzoyl or the monobenzoyl compound, a substance was obtained which on analysis gave figures agreeing with a compound formed by the loss of a

molecule of water from one molecule of the monobenzoyl compound and one molecule of the picric acid. On heating with potassium hydroxide, this compound regenerated the base. Phenol itself and *o*- and *p*-nitrophenol yield compounds with benzoyldianilinostilbene, and it is proposed to investigate these compounds more fully later.

#### EXPERIMENTAL.

The reactions under investigation took place quite consistently, and with care, uniform yields of the two primary products (dibenzoyldianilinostilbene,  $C_{40}H_{30}O_2N_2$ , and 1:2:4:5-tetraphenylglyoxaline) were readily obtained.

The heating was carried out in conical Jena-glass flasks fitted with air condensers. The boiling mixture was generally seeded with a few crystals of dibenzoyldianilinostilbene.

The flasks containing the mixtures were heated in an air-bath kept at 150–160°. An air-bath was found most suitable for this purpose, because, in order to obtain the best results, the mixtures had to be kept just boiling. Whenever the mixture was, either, not kept boiling, or was allowed to boil too vigorously, excessive charring resulted, and the yield fell. It was found that the temperature requisite to secure slow boiling varied with the time, and that two exactly parallel experiments proceeded at different rates. By using an air-bath, and regulating the distance of the flasks from the bottom of the bath, it was possible to overcome these difficulties.

In the hope that the results obtained might lead to the elucidation of the changes taking place and to the determination of the substances that really take part in the reaction, a series of comparative experiments was made, employing different combinations of the materials; in each case the yield of dibenzoyldianilinostilbene was noted.

From the results of these experiments it was deduced in colour-order to obtain dibenzoyldianilinostilbene, both aniline and benzaldehyde must be present, and, further, alcohol, methyl were present in molecular proportions, the yield was acid (in which as that obtained if two molecules of the cyanohydrin position), very the aniline were employed. Further, it was found benzene. It does obtained in the latter case was much the same as that when aniline, benzaldehyde, and benzaldehydecyanohydrin a series of molecular proportions, were employed. Finally, no yield was obtained by increasing the ratio of the cyanostilbene, aniline beyond the ratio of two to one. All these conclusions were verified by the later investigations, which have shown that dibenzoyldianilinostilbene molecule there exist two aniline residues for every aniline residue.

Experiments were also carried out on the action of continued heating on benzaldehydecyanohydrin and on phenylanilinoacetonitrile. In the former case great charring took place, and nothing but benzoic acid could be isolated. In the latter case a quantity of dibenzoyldianilinostilbene was obtained, and the tars remaining after the removal of this substance were further examined. By steam distillation there was obtained from them a quantity of an oil (which proved to be aniline), together with a smaller quantity of benzylideneaniline. This showed that the nitrile on heating underwent decomposition into hydrocyanic acid and benzylideneaniline. The latter substance was then hydrolysed; the aniline thus produced, not being required for the further reaction, remained behind, whilst the benzaldehyde formed entered into reaction to furnish the second aldehyde residue, shown by the other experiments to be at least advantageous, if not absolutely necessary, for the production of dibenzoyldianilinostilbene.

*Dibenzoyldianilinostilbene*,  $C_{40}H_{30}O_2N_2$ .

Although this was originally obtained by the prolonged action of heat on a mixture of benzylideneaniline (1 mol.) and benzaldehydecyanohydrin (2 mols.), it was found that the best method of preparation consisted in heating together aniline (1 mol.) with benzaldehydecyanohydrin (2 mols.). If these two substances were employed in molecular proportions, and one molecular part of benzaldehyde was added, almost as good a yield was obtained, but the isolation of the other products of the reaction was complicated by the excess of benzaldehyde remaining at the end of the reaction.

may be. Aniline and benzaldehydecyanohydrin are heated together for an hour at  $150-160^\circ$ , a quantitative yield of phenylanilinoacetonitrile can be obtained, but the heating was generally continued

If, however, isolation of this compound. No apparent change in difficulty in experiment the elimination of water required by this reaction both in solution and the close of the second day's heating (forty-eight

All attempts at quiet boiling changed to a crackling. Soon after this resulted in the observed, crystals began to separate from the same salts and continued to do so until the whole was interlaced with the only semi-solid mass. The yield generally reached its maximum by preparation four to thirty hours after the separation of the crystals

Benzoyl was 25-40 per cent. of the theoretical. hydrochlorine requisite for the reaction was found to vary considerably. In some cases one hundred and twenty hours' heating was necessary to obtain a good yield, whilst occasionally an equally good yield was obtained after only forty-eight hours' heating. Many

experiments were carried out with the object of observing some connexion between the length of heating and the yield obtained, but they proved unsuccessful. Considerable experience is requisite in order to obtain good yields without charring and in reasonable time, but when this has been acquired, regular, good, and clean yields are readily obtained. During the early part of the heating a considerable quantity of hydrocyanic acid was liberated.

To separate the substance from the adhering tars, the contents of the flasks were either (a) mixed while warm with sufficient pure ether to produce a mobile liquid, and the crystals were collected and washed, or (b) allowed to remain overnight with ether equal in volume to three times that of the tars; after keeping, the substance was deposited as a crystalline mass, which was collected and washed. The tars obtained in these processes were kept for further treatment (p. 1762).

The crude dibenzoyldianilinostilbene obtained by this method was usually mixed with some tetraphenyglyoxaline; the quantity of glyoxaline was found to increase with the time of heating requisite in the preparation.

The dibenzoyldianilinostilbene was present in well-formed crystals, often of some considerable size, in which case they were found to be hard and brittle. Its complete separation was achieved by extracting the mixture in a Soxhlet apparatus with dry ether (free from alcohol); dibenzoyldianilinostilbene was insoluble, whilst tetraphenyglyoxaline was sparingly soluble in that solvent. To ensure a pure product all the lumps were crushed before extraction and occasionally during the process. The glyoxaline, if present to any considerable extent, separated in hard, granular crystals from the ether.

*Dibenzoyldianilinostilbene*, after purification by this means, was recrystallised from amyl alcohol, from which it separated in colourless, glistening, needle-shaped crystals, having a melting point well above  $350^{\circ}$ . It was fairly readily soluble in ethyl alcohol, methyl alcohol, or chloroform, very soluble in glacial acetic acid (in which solution, however, it was found to undergo decomposition), very sparingly so in acetone, and insoluble in ether or benzene. It does not crystallise well from solvents of low boiling point.

At first it was thought that this substance yielded a series of well-defined salts, but further investigation showed them to be salts of the decomposition product, monobenzoyldianilinostilbene,  $C_{23}H_{26}ON_2$ . By the action of acids or of alkalis, dibenzoyldianilinostilbene was found to undergo decomposition:

0.3020 gave 0.9295  $CO_2$  and 0.1500  $H_2O$ . C=83.94; H=5.52.  
0.3015 „ 0.9300  $CO_2$  „ 0.1505  $H_2O$ . C=84.12; H=5.55.

0.2935 gave 12.95 c.c.  $N_2$  (moist) at  $19.5^\circ$  and 734 mm.  $N=4.98$ .  
 0.3000 „ 13.40 c.c.  $N_2$  „ „  $16.5^\circ$  „ 738.5 mm.  $N=5.12$ .  
 $C_{40}H_{30}O_2N_2$  requires  $C=84.21$ ;  $H=5.26$ ;  $N=4.91$  per cent.

Dibenzoyldianilinostilbene was also prepared by heating together the benzoyl derivative of  $\alpha$ -keto- $\beta$ -anilino- $\alpha\beta$ -diphenylethane (1 mol.), aniline (1 mol.), and potassium cyanide ( $\frac{1}{2}$  mol.). After eighteen hours' heating, the substance separated, and was treated as described in the other method of preparation. From the tars in this preparation, benzanilide was obtained, but no trace could be obtained of benzildianil.

*Dibenzoyldianilinostilbene methiodide*,  $C_{40}H_{30}O_2N_2, MeI$ , was prepared by adding a 50 per cent. solution of methyl iodide in absolute alcohol, drop by drop, to a solution of the dibenzoyl compound also in absolute alcohol. The methiodide was precipitated as a colourless, crystalline powder. It was insoluble in all ordinary organic solvents, and did not melt below  $350^\circ$ . If heated above that temperature, it charred and emitted fumes.

For analysis, the substance was prepared from a pure specimen of the dibenzoyl compound, and the resulting product was extracted twice with boiling absolute alcohol:

0.2623 gave 0.0863 AgI.  $I=17.78$ .

$C_{41}H_{33}O_2N_2I$  requires  $I=17.84$  per cent.

*Monobenzoyldianilinostilbene*,  $C_{33}H_{26}ON_2$ .

Dibenzoyldianilinostilbene, when treated with acids, gave what were at first supposed to be true salts, but analysis proved that this was not the case. Further, on treating these salts with alkali, the original substance was not regenerated, but a yellow solid was obtained. This yellow solid could also be obtained by boiling dibenzoyldianilinostilbene with  $N/2$ -aqueous potassium hydroxide with the addition of a few drops of alcohol. It was found to be the true base corresponding with the above-mentioned salts. It was unstable in all solvents except alcohol, and in that solvent it was so sparingly soluble that recrystallisation was impossible. The yellow base was prepared for analysis by dissolving the pure dibenzoyldianilinostilbene in alcohol, adding  $N/2$ -aqueous potassium hydroxide drop by drop until a precipitate just began to form, and cooling the mixture, when the product separated in small, glistening crystals, melting at  $212^\circ$ , which were ground, boiled with water, and then washed with alcohol and ether:

0.2347 gave 0.7283  $CO_2$  and 0.1201  $H_2O$ .  $C=84.63$ ;  $H=5.69$ .

0.1799 „ 9.50 c.c.  $N_2$  (moist) at  $15^\circ$  and 729.5 mm.  $N=5.91$ .

$C_{33}H_{26}ON_2$  requires  $C=84.98$ ;  $H=5.58$ ;  $N=6.01$  per cent.

The fact that a benzoyl group had been eliminated in this reaction was shown by the precipitation of benzoic acid on acidification of the filtrate from the monobenzoyl compound. In order that this decomposition might be caused to yield an estimate of the molecular weight of the original dibenzoyl compound, the reaction was carried out quantitatively.

Three to four grams of the substance were heated under reflux, with 25 c.c. of *N*-aqueous potassium hydroxide in the presence of a little alcohol. The product was collected, washed, and weighed. The excess of alkali was estimated in the filtrate:

3.556 gave 0.765 benzoic acid and 2.82 base.

The equation  $C_{40}H_{30}O_2N_2 + KOH = C_{33}H_{26}ON_2 + C_7H_5O_2K$  requires 0.762 benzoic acid and 2.90 base.

A colourless modification of monobenzoyldianilinostilbene was obtained in an attempt to recrystallise the yellow variety from alcohol by spontaneous evaporation of the solvent; it crystallised in feathery, colourless crystals. This product, on heating, was found to change into the yellow form at about 160–180°, and then melted at 212°. It gave the same salts as the yellow modification.

*Benzoyldianilinostilbene hydrochloride* crystallised from acetic acid or from alcohol in colourless crystals, melting above 350°. When heated on platinum foil, the substance melted with decomposition and evolution of gas. The base could be regenerated by warming with potassium hydroxide or carbonate:

0.2326 gave 0.0866 AgCl. Cl = 9.21.

$(C_{33}H_{26}ON_2)_3 \cdot 4HCl$  requires Cl = 9.20 per cent.

The *platinichloride*, prepared in the usual way, was washed with glacial acetic acid and water, and dried:

0.4125 gave 0.0727 Pt. Pt = 17.62.

$(C_{33}H_{26}ON_2)_3 \cdot 4HCl \cdot (PtCl_4)_2$  requires Pt = 17.58 per cent.

The *acetate*,  $C_{33}H_{26}ON_2 \cdot 2C_2H_3O_2$ , was recrystallised from water, and formed colourless, needle-shaped crystals, melting at 335°:

0.2205 gave 0.6110 CO<sub>2</sub> and 0.1210 H<sub>2</sub>O. C = 75.74; H = 6.11.

$C_{37}H_{34}O_5N_2$  requires C = 75.77; H = 5.80 per cent.

#### *Compounds formed by Benzoyldianilinostilbene with Phenols.*

*Compound with Picric Acid*,  $C_{33}H_{26}ON_2 \cdot C_6H_2(NO_2)_3$ .—This was prepared by adding a hot concentrated solution of picric acid in glacial acetic acid or alcohol to a solution of the benzoyl compound (or of the dibenzoyl compound) in the same solvent. The product was recrystallised from methyl or ethyl alcohol, when it separated in slender, silky needles, melting at 274.5°.

When this substance was boiled with aqueous potassium



hydroxide in presence of a few drops of alcohol, the base was regenerated. Potassium carbonate, however, did not bring about this decomposition.

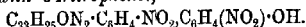
Analyses showed that this substance was not a true picrate, but was a compound resulting by the elimination of a molecule of water from one molecule of the base and one of picric acid:

0.2003 gave 0.5066  $\text{CO}_2$  and 0.0715  $\text{H}_2\text{O}$ .  $\text{C}=68.98$ ;  $\text{H}=3.98$ .

0.2000 „ 18.40 c.c.  $\text{N}_2$  (moist) at  $19^\circ$  and 722.9 mm.  $\text{N}=10.23$ .

$\text{C}_{38}\text{H}_{27}\text{O}_7\text{N}_5$  requires  $\text{C}=69.13$ ;  $\text{H}=3.99$ ;  $\text{N}=10.34$  per cent.

*Compound with o-Nitrophenol,*



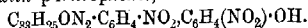
—This cannot be prepared in solution, but was readily obtained by heating together rapidly the two components until the whole mass became liquid and the vigorous evolution of water had ceased. The molten mass was poured into about twice its own volume of methylated spirit. It was recrystallised from a mixture of three parts of methyl alcohol and two parts of water, and separated in orange-yellow, hexagonal plates, melting at  $183^\circ$ , with the production of a deep red substance, which became solid and melted between  $250^\circ$  and  $300^\circ$ . This red compound could be obtained from the original substance by crystallisation from a mixture of chloroform and light petroleum, when it did not melt below  $350^\circ$ . On crystallising the red substance from methyl or ethyl alcohol, the orange-yellow compound was obtained.

Analysis of the substance recrystallised from alcohol gave:

0.2004 gave 0.5459  $\text{CO}_2$  and 0.0861  $\text{H}_2\text{O}$ .  $\text{C}=74.29$ ;  $\text{H}=4.77$ .

$\text{C}_{45}\text{H}_{34}\text{O}_6\text{N}_4$  requires  $\text{C}=74.38$ ;  $\text{H}=4.68$  per cent.

*Compound with p-Nitrophenol,*



—This was prepared in the same way as the o-nitrophenol compound, and was recrystallised from the same solvent, from which it was deposited in clusters of lemon-yellow, hexagonal plates, melting at  $210-212^\circ$ . This compound showed no change on melting:

0.2092 gave 0.5705  $\text{CO}_2$  and 0.0890  $\text{H}_2\text{O}$ .  $\text{C}=74.38$ ;  $\text{H}=4.73$ .

$\text{C}_{45}\text{H}_{34}\text{O}_6\text{N}_4$  requires  $\text{C}=74.38$ ;  $\text{H}=4.68$  per cent.

*Compound with Phenol,  $\text{C}_{38}\text{H}_{25}\text{ON}_2 \cdot \text{C}_6\text{H}_5, 2\text{C}_6\text{H}_5 \cdot \text{OH}$ .*—This was prepared in the same way as the compounds with the nitrophenols, and was recrystallised, first from methylated spirit, and then from absolute alcohol, when it formed colourless crystals, melting at  $226^\circ$ :

0.2279 gave 0.6955  $\text{CO}_2$  and 0.1229  $\text{H}_2\text{O}$ .  $\text{C}=83.24$ ;  $\text{H}=5.99$ .

0.1932 „ 6.60 c.c.  $\text{N}_2$  (moist) at  $10.0^\circ$  and 722.9 mm.  $\text{N}=3.92$ .

$\text{C}_{51}\text{H}_{41}\text{O}_3\text{N}_2$  requires  $\text{C}=83.84$ ;  $\text{H}=5.75$ ;  $\text{N}=3.84$  per cent.

*Decompositions of Benzoyldianilinostilbene.*

Benzoyldianilinostilbene was found to be very unstable when in solution or when heated.

*In Solution.*—When the substance was dissolved in chloroform, light petroleum, benzene, amyl alcohol, or acetone, and allowed to remain exposed to the air at the ordinary temperature, the pale yellow solution first obtained gradually darkened; thus, in chloroform solution the colour was found to have darkened very appreciably in one hour, and even less if the solution was kept warm. At the end of a day or so the solution became deep brown, and, if the solution was concentrated, crystals separated, which, on recrystallisation, melted at  $163^{\circ}$ , and proved to be benzanilide.

From the filtrate, after the separation of the benzanilide, a second substance was isolated by concentrating the solution to a pasty mass, and then adding sufficient methylated spirit to dissolve the residue when boiled. After filtration and cooling, the solution deposited long, needle-shaped crystals, which, after recrystallisation, melted at  $163^{\circ}$ . This substance was proved to be dibenzoylaniline by analysis (Found,  $C=79.14$ ;  $H=5.04$ ;  $N=4.67$ . Calc.,  $C=79.7$ ;  $H=4.98$ ;  $N=4.65$  per cent.), and by a mixed melting-point determination. Hence in solution benzoyldianilinostilbene undergoes oxidation, yielding benzanilide and dibenzoylaniline. No other product could be isolated.

*By Heat.*—Benzoyldianilinostilbene, on being heated to  $120$ – $140^{\circ}$  for a short time, was transformed into a jelly-like mass, which, on cooling, became quite brittle, and had a dirty yellowish-brown colour. On extracting the mass for a short time with benzene, some of it dissolved, and there remained a white, powdery residue, which did not melt below  $350^{\circ}$ , and proved to be dibenzoyldianilinostilbene. This was proved by the fact that with potassium hydroxide it yielded benzoic acid and monobenzoyldianilinostilbene. The benzene solution deposited crystals of benzanilide.

If instead of extracting the mass with benzene, ether was used, then from the filtrate a yellow substance separated, which, on recrystallisation from alcohol or ether, yielded well-formed crystals, melting at  $145$ – $147^{\circ}$ . This substance was shown to be benzildianil by its ready hydrolysis with acids to benzil and aniline (Siegfeld, *Ber.*, 1892, 25, 2601). Benzildianil was also obtained in small quantities by heating together  $\alpha$ -keto- $\beta$ -anilino- $\alpha\beta$ -diphenylethane and aniline. Hence by the action of heat, benzoyldianilinostilbene yields dibenzoyldianilinostilbene, benzildianil, and benzanilide.

1:2:4:5-Tetraphenylglyoxaline,  $C_{27}H_{20}N_2$ 

As has been stated, crude dibenzoyldianilinosilbene is mixed with this glyoxaline, the identity of which has been established by synthesis (Everest and McCombie, *loc. cit.*).

When the tars from which dibenzoyldianilinosilbene had been obtained were further heated, another small quantity of this substance was produced, together with a considerable quantity of the glyoxaline; indeed, if the original reaction had been allowed to proceed to completion, the product on further heating was almost entirely the glyoxaline. The glyoxaline was separated from the residual tars by means of ether, and was thus obtained directly in a crystalline condition. It was recrystallised from methylated spirit, and melted at  $215^{\circ}$ . (Found,  $C=86.72$ ;  $H=5.41$ ;  $N=7.41$ . Calc.,  $C=87.1$ ;  $H=5.38$ ;  $N=7.53$  per cent.) The general properties of this substance have already been described by us (*loc. cit.*).

 $\alpha$ -Keto- $\beta$ -anilino- $\alpha\beta$ -diphenylethane,  $C_{20}H_{17}ON$ .

This substance was isolated on several occasions, but not regularly, from the residual tars after the separation of dibenzoyldianilinosilbene. It was always obtained when that substance had separated earlier than usual, and when in such cases, the tars were allowed to remain, sometimes merely overnight, sometimes for several days. There seems every reason to believe that  $\alpha$ -keto- $\beta$ -anilino- $\alpha\beta$ -diphenylethane is a regular constituent of the tars at this period of the reaction, and that its well known property of remaining in a supercooled condition accounts for its being isolated only occasionally.

The crystals were collected, washed with ether, and recrystallised from methylated spirit, when they melted at  $98^{\circ}$ . (Found,  $C=83.58$ ;  $H=6.05$ ;  $N=5.04$ . Calc.,  $C=83.63$ ;  $H=5.92$ ;  $N=4.88$  per cent.) The substance gave a hydrochloride melting at  $200-202^{\circ}$  (Lachowicz, *Monatsh.*, 1893, **14**, 280, gives  $183^{\circ}$ ), an acetyl derivative melting at  $153^{\circ}$ , and with alcoholic potassium hydroxide it gave a purple-violet coloration. Finally, a mixed melting-point determination with a synthetic specimen proved them to be identical.

## Benzanilide.

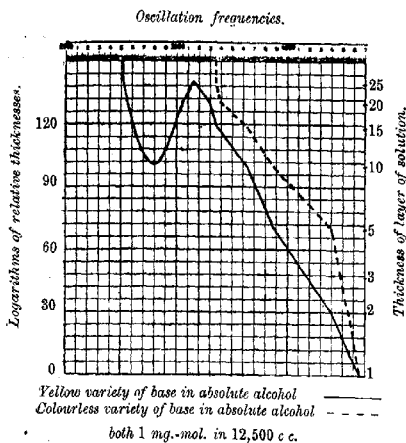
This was met with in the tars from the original reaction that had been kept for several weeks. A crystalline deposit was noticed,  $O$ -rich, on recrystallisation, proved to be mainly tetraphenyl- $C_{61}H_{41}N_2$ , but after this had separated the mother liquors deposited

shining, plate-like crystals (m. p.  $160^{\circ}$ ), which were shown to be benzanilide.

*Absorption Spectra of Benzoyldianilinostilbene and of its Salts.*

With the view of obtaining some insight into the relationships between the two forms of this base and its salts, a series of photographs was taken of the absorption spectra of these in solution. The solutions used were molecularly equivalent, and contained about 1 millimole per 12,500 c.c.

The two forms of the base showed very different absorptions, as shown in the diagram. The yellow variety showed a distinct band



near the visible end of the spectrum, together with general absorption in the regions more remote from the visible end. There was no fluorescence shown at the end of the tube during exposure.

The colourless variety, which was free from halogen, exhibited no band at all, but showed general absorption at the end of the spectrum furthest from the visible. Bright fluorescence was observed during exposure.

The hydrochloride showed identical absorption with that of the colourless variety of the base. It also showed the same bright fluorescence.

If a few drops of concentrated hydrochloric acid were added to the solution of the yellow variety, then the spectrum shown was that of the hydrochloride, and fluorescence was observed. If, on the

other hand, a few drops of aqueous potassium hydroxide were added to a solution of the colourless variety, the absorption spectrum showed that a considerable portion (but not all) of the base had been converted into the yellow variety. The band characteristic of the yellow form had become developed, but was not so distinct as in the case of the pure yellow form. Furthermore, the fluorescence, although greatly weakened, was still visible. This solution was not found to change on keeping.

From these results it appears evident that the salts which are colourless are the salts, not of the yellow base, but of its colourless modification.

We desire to thank Dr. C. K. Tinkler for his kind assistance in the spectroscopic portion of this work.

THE UNIVERSITY, EDGBANTON,  
BIRMINGHAM.

### CXCVIII.—*Composition of the Essential Oil of Myrica Gale, L.*

By SAMUEL SHROWDER PICKLES.

BOG MYRTLE or sweet gale (*Myrica Gale, L.*) is a well known shrub, varying in height from 2 to 5 feet, which occurs in marshy and moorland districts in Northern and Arctic Europe, Asia, and America. It is abundant in Scotland, northern England, and Ireland, and also occurs, although more rarely, in the south and east of England.

The plant contains a volatile oil, which has a characteristic odour. Mention is made of the "fragrant gale" or "bog myrtle" by several of the English classical writers, and in Scotland the sweet gale has long been the badge of the Campbells.

The shrub is known by various names in different countries. It is the "bay bush" of North America, and is also known as "willow myrtle" and Dutch myrtle.

The essential oil of *Myrica Gale* does not seem to have had any extensive application. The plant itself was formerly employed as a drug under the name "herba myrti brabanti," but is no longer used in medicine. Dr. J. Chevalier has recently found that the essential oil acts as a powerful purgative (*Bulletin, Roure Bertrand Fils*, April, 1910, p. 57). The bark of the plant is said to yield a

tannin, and the flower buds are stated to contain a yellow colouring matter (Engler and Prantl).

The oil appears to have been first examined by Rabenhorst in 1837 (Gildemeister and Hoffmann, *Volatile Oils*, p. 331), who found that, on distillation, the leaves of *M. Gale* yielded 0.65 per cent. of a brownish-yellow oil, having D 0.876. It is also stated that at 17.5° the oil congeals partly, and at 12.5° completely, to a crystalline mass, and that it contains 70 per cent. of camphor (?) (*loc. cit.*). A more recent examination has been made by Messrs. Roure Bertrand Fils (see *Bulletin*, April, 1910, p. 55), who determined the usual physical and chemical constants of the oil obtained from the branches.

There seems, however, to be no information on record regarding the chemical constituents of the oil, and so, having a small quantity of oil at his disposal, the author decided to identify, as far as possible, the component substances.

The bog myrtle from which the oil described in the present paper was derived was collected for Professor Dunstan in Argyllshire, N.B., and at his suggestion the author undertook the extraction and examination of the oil.

Two consignments of raw material have been examined, both of which were obtained from Argyllshire. The first consisted of about 30 lbs. of leaves and stems, and contained a rather large proportion of stems. The material had a slight herb-like odour somewhat suggestive of sage.

For the extraction of the oil the material was first cut up in a chaff-cutting machine, and then subjected to distillation in steam. The yield of oil from this consignment of the plant was found to be 0.076 per cent. The oil was pale yellow, had a characteristic, pleasant odour recalling that of sage, but somewhat more camphoraceous. On dilution with alcohol, or on remaining for some time in the cold, a solid material separates in colourless, shining, leafy crystals.

The second specimen, received at a later date, consisted of 42½ lbs. of bog myrtle, mainly leaves, the twigs being present to a small extent only. The leaves had the pleasant characteristic odour, and were partly dry. The yield of oil on distillation was 43 c.c., or 39.2 grams = 0.203 per cent.

The two oils thus obtained differed slightly in their physical and chemical characters, as will be seen from the following table. For comparison, the corresponding values obtained by Messrs. Roure Bertrand Fils for the oil from the branches of *M. Gale* are included.

	Oil from leaves and twigs.	Oil mainly from leaves.	Oil from branches. (Roure Bertrand Fils.)
Yield per cent. ....	0.076	0.203	0.045
Sp. gr. at 15° .....	0.915	0.912	at 25° = 0.8884
$n_D^{20}$ (100 mm. tube).....	5.17'	11.26'	5.16'
Acid value .....	7.0	4.0	3.48
Total saponification value .....	31.7	23.2	17.98
Ester value .....	24.7	19.2	14.50
Saponification value of acetylated oil...	—	56.4	50.23

#### Identification of the Constituents of the Oil.

For this purpose the oil obtained mainly from the leaves was subjected to examination. It has been stated that on cooling, or on addition of alcohol, a crystalline substance separates from the oil. To this is probably due the statement in the earlier work on the subject that the oil contains 70 per cent. of camphor. This latter should not be taken to mean the camphor of to-day, as this statement was probably made when the term "camphor" was applied to any solid substance separating from an oil. In any case, however, the amount present was considerably over-estimated. Messrs. Roure Bertrand Fils more correctly consider the separation of solid matter to be due to the presence of paraffins in the oil, but do not give any evidence in support of this conclusion.

In order to separate this constituent as far as possible, the oil (20 c.c.) was first cooled in a freezing mixture, and an equal volume of methyl alcohol was added. The crystalline solid which separated was collected, and washed with a little more methyl alcohol. It was then treated with a concentrated solution of sodium hydroxide for some time in order to remove entirely any acids, phenols, etc., and the undissolved material was finally dissolved in ether, from which it recrystallised in shining leaflets, melting at 63–64°.

This substance is apparently quite pure; it is almost insoluble in acetic anhydride, is not affected by potassium permanganate solution, and is scarcely acted on by sulphuric acid.

It is apparently a paraffin, having probably the composition  $C_{29}H_{60}$ . The quantity obtained from 20 c.c. oil was not more than 0.15 gram (about 0.75 per cent.). It is worthy of note that similar, if not identical, hydrocarbons have been found in the oils from certain *Pelargonium*, spp., *Cistus monspeliensis*, caraway (*Carum Carvi*, L.), dill (*Anethum graveolens*), *Arnica montana*, Indian hemp, etc.

The oil from which the solid portion had been removed was subjected to the following treatment. The methyl alcohol was removed by distillation and washing. The oil was then mixed with several volumes of ether, and the ethereal solution repeatedly

extracted with aqueous sodium carbonate solution. On acidifying the aqueous solution, a considerable quantity of solid material separated, which, after removal, drying, and recrystallising from alcohol, was obtained in glistening crystals, melting at  $62^{\circ}$ . It consisted almost entirely of palmitic acid.

The ethereal solution of the oil was afterwards treated with sodium hydroxide solution, but only a trace of indefinite material was removed by this means, and a subsequent treatment of the oil with sodium hydrogen sulphite solution also failed to separate any appreciable quantity of aldehydes or ketones.

After the removal of the ether the oil was subjected to distillation under diminished pressure, when the following fractions were obtained: (1) Small fraction, b. p.  $76^{\circ}/35$  mm. (2) Fraction below  $110^{\circ}/20$  mm. (3) Fraction  $110-150^{\circ}/20$  mm. (4) Fraction  $150-165^{\circ}/20$  mm. (5) Residue.

Fraction (1) had a pronounced odour of cineole, and the presence of this substance was definitely proved by the formation of its compound with tetraiodopyrrole (m. p.  $112-114^{\circ}$ ). The cineole-tetraiodopyrrole compound is stated to melt at  $112^{\circ}$ .

Fraction (2) was redistilled under atmospheric pressure, when it was found to boil for the most part below  $176^{\circ}$ . The distillate had a terpene-like odour, together with that of cineole:

0.1210 gave 0.3770  $\text{CO}_2$  and 0.1260  $\text{H}_2\text{O}$ .  $\text{C} = 85.0$ ;  $\text{H} = 11.6$ .

This result seemed to indicate the presence of terpenes, together with cineole, and the presence of dipentene in this fraction was proved by the formation of dipentene tetrabromide. This was deposited from the oil in colourless plates after bromination, and when recrystallised from ethyl acetate melted at  $124-125^{\circ}$ .

The fractions of higher boiling point were first boiled with alcoholic potassium hydroxide to hydrolyse the esters present, and there was recovered from the potassium salts formed in this process a mixture of fatty acids insoluble in water. These acids, present in the oil in the form of esters, could not be separated and identified with certainty on account of the small quantity obtained. They were apparently of fairly high molecular weight, possibly nonoic or closely related acids.

After hydrolysis the oil was again fractionated: (1) Very small fraction, b. p.  $180-220^{\circ}$ . (2) Pale green liquid, b. p.  $258-268^{\circ}$ . (3) Pale blue liquid, b. p.  $268-285^{\circ}$ . (4) Residue of high boiling point.

Fraction b. p.  $180-220^{\circ}$ :—This had a somewhat menthol-like odour suggestive of a terpene alcohol:

0.1425 gave 0.4250  $\text{CO}_2$  and 0.1460  $\text{H}_2\text{O}$ .  $\text{C} = 81.4$ ;  $\text{H} = 11.4$ .

$\text{C}_{10}\text{H}_{18}\text{O}$  requires  $\text{C} = 77.9$ ;  $\text{H} = 11.7$  per cent.



This fraction probably consists of a terpene-alcohol mixed with a small proportion of terpenes. The quantity was, however, too small to attempt a separation, and attempts to obtain crystalline derivatives of the alcohol were unsuccessful.

*Fraction b. p. 258—268°:*—This was a pale green liquid, which yielded the following results on analysis:

0.1455 gave 0.4380  $\text{CO}_2$  and 0.1465  $\text{H}_2\text{O}$ .  $\text{C}=82.1$ ;  $\text{H}=11.2$ .

It had a pleasant, persistent odour, and it is to this fraction and the succeeding one, together with cineole, that the characteristic odour of the oil is due. A methoxyl determination was made on a portion of this fraction, but no methyl iodide was liberated.

*Fraction b. p. 275—285°:*—This was a fairly mobile liquid, having a pale blue colour and a pleasant odour:

0.1230 gave 0.3770  $\text{CO}_2$  and 0.1270  $\text{H}_2\text{O}$ .  $\text{C}=83.6$ ;  $\text{H}=11.5$ .

The two fractions b. p. 258—268° and b. p. 268—285° constitute about one-half of the total oil, and consist essentially of a sesquiterpene mixed with an oxygenated constituent, probably a higher alcohol.

On treatment of these fractions with hydrogen chloride only liquid hydrochlorides could be obtained. Unfortunately the small quantity of oil available did not allow of a more complete examination of this portion of the oil.

#### Summary.

The solid material which separates from the oil of *Myrica Gale* on cooling consists of a paraffin hydrocarbon, m. p. 63—64°, and probably having the formula  $\text{C}_{29}\text{H}_{60}$ , which is present to the extent of about 0.75 per cent.

The oil also contains (1) about 2.5 per cent. of free fatty acids, principally palmitic acid; (2) terpenes, including dipentene; (3) cineole; (4) esters of fatty acids; (5) probably a mixture of alcohols of high boiling point, and (6) a sesquiterpene.

The cineole and terpenes constitute approximately 50 per cent. of the oil.

CXCIX.—*An Application of Kirchhoff's Equation to Solutions. (A Contribution to the Thermodynamic Theory of Solubility.)*

By ROBERT TAYLOR HARDMAN and JAMES RIDDICK PARTINGTON.

On the basis of his theory of solution, van't Hoff (*Kongl. Svenska. Akad. Handl.*, 1885, **21**, 38) deduced a general differential equation, applicable to solutions of all concentrations, which connects the osmotic pressure,  $P$ , of a saturated solution with  $\lambda^1$ , the latent heat of reversible dissolution in a saturated solution:

$$\frac{dP}{dT} = \frac{\lambda^1}{T\Delta V} \quad \dots \quad (1)$$

$\Delta V$  = change of total volume occurring when enough solvent transpires through a semipermeable diaphragm to dissolve a gram-molecule of solute. If the system is maintained at a constant temperature  $T$ , and the external work  $P\Delta V$  is done by the osmotic pressure,  $\lambda^1$  is the heat absorbed in the process.

If  $\lambda$  is the heat absorbed when a molecule of solute dissolves in sufficient solvent to produce a saturated solution, so that no external work is done (say, by mixing the components in a calorimeter), then:

$$\lambda = \lambda^1 - P\Delta V \quad \dots \quad (2)$$

Let us now assume that the osmotic pressure conforms to the laws of dilute solutions, so that:

$$P = \xi RT \quad \dots \quad (3)$$

where  $\xi$  = the volumetric molecular concentration of the solution, or the number of gram-molecules of solute per unit volume. By definition:

$$\xi = 1/\Delta V \quad \dots \quad (4)$$

$$\therefore \frac{d \ln \xi}{dT} = \frac{\lambda}{RT^2} \quad \dots \quad (5)$$

which is the general differential equation for saturated dilute solutions. The differential coefficients in (1) and (5) are total, since  $P$  and  $\xi$  are, under the conditions imposed, functions of  $T$  alone.

The integration of (5) was effected by van't Hoff on the assumption that  $\lambda$  may be regarded as sensibly constant over a small range of temperature  $T_2 - T_1$ , in which case one readily finds:

$$\ln \frac{\xi_2}{\xi_1} = \frac{\lambda}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad \dots \quad (6)$$

an equation which gave satisfactory results in its own restricted

field (van Deventer and van der Staadt, *Zeitsch. physikal. Chem.*, 1892, 9, 54; van Marsevan, *ibid.*, 1895, 25, 91; Noyes and Sammet, *ibid.*, 1903, 43, 513). But if the range of temperature is not very small, the assumption about the constancy of  $\lambda$  is invalid.

The present authors have sought to extend the application of (5) to fairly large intervals of temperature, and for this purpose have utilised the well-known theorem of Kirchhoff (*Pogg. Ann.*, 1858, 103) to the effect that the rate of increase of the heat of reaction, taken positive for heat absorbed, with the temperature at which a reaction proceeds, is equal to the total heat capacity of the system of products minus the total heat capacity of the system of initial substances:

$$\frac{dQ}{dT} = \Gamma^1 - \Gamma \quad \dots \quad (7)$$

Let  $s$  grams of solute saturate 100 grams of solvent, and let  $c_1$ ,  $c_2$ ,  $c$  be the specific heats of solute, solvent, and solution respectively. If  $Q$  is the heat absorbed in the calorimetric process:

$$\frac{dQ}{dT} = (s + 100)c - (sc_1 + 100 c_2) \quad \dots \quad (8)$$

The heat of solution increases, remains constant, or decreases with rise of temperature, according as:

$$(s + 100)c \begin{cases} \geq \\ < \end{cases} (sc_1 + 100 c_2) \quad \dots \quad (9)$$

It appears that the lower inequality usually obtains.

If  $l$  is the heat absorbed when 1 gram of solute forms a saturated solution:

$$Q = sl \quad \dots \quad (10)$$

$$\therefore \frac{dl}{dT} = \frac{100 + s}{s} c - \frac{sc_1 + 100 c_2}{s} \quad \dots \quad (11)$$

Now  $c_1$ ,  $c_2$ ,  $c$  may be assumed to be sensibly independent of temperature, so that:

$$\begin{aligned} l &= l_0 + \frac{100 + s}{s} cT - \frac{sc_1 + 100 c_2}{s} T \\ &= l_0 + (c - c_1) T + \frac{100(c - c_2)}{s} T \quad \dots \quad (12) \end{aligned}$$

where  $l_0$  is an integration constant.

Now it has been shown experimentally by Schüller (1869), Thomsen (1870), and Marignac (1871-76) that the difference between the specific heats of the solution and solvent, in the case of dilute aqueous solutions, tends on increasing dilution to become proportional to the concentration. Assuming, therefore, in general:

$$c = c_2 + ks \quad \dots \quad (13)$$

where  $k$  may be positive or negative, we have:

$$l = l_0 + (a_1 + a_2)T = l_0 + aT,$$

where  $a_1 = c - c_1$ ,  $a_2 = k$ ,  $a = a_1 + a_2$ , are constants.  $a$  is usually negative.

For a mol. ( $M$  grams) of solute we have:

$$\lambda = Ml = \lambda_0 - aT \quad (14)$$

where  $a = -Ma$  is a constant.

The heat of solution is therefore a linear function of the temperature, and behaves similarly to the latent heat of evaporation of a pure liquid.

If we substitute (14) in (5), and integrate, we obtain:

$$\ln \xi = \int \frac{\lambda_0 - aT}{RT^2} dT = -\frac{\lambda_0}{RT} - \frac{a}{R} \ln T + C \quad (15)$$

where  $C$  is the integration constant.

The (hypothetical) physical significance of  $\lambda_0$  and  $C$  is found by setting  $T=0$  in (14) and (15) respectively.

If we collect the constants, and multiply through by the modulus of the ordinary logarithms, we find:

$$\log \xi = A^1 - \frac{B}{T} - C \log T \quad (16)$$

where  $A^1$ ,  $B$ ,  $C$  are constants:

$$B = -\frac{\lambda_0}{R} \times 2.3026, C = \frac{M(a_1 + a_2)}{R} \times 2.3026.$$

If  $\rho$  is the density of the solution, which we shall suppose does not differ appreciably from that of the pure solvent:

$$\xi = \frac{s\rho}{100M} \quad (17)$$

$$\therefore \log s = A - \frac{B}{T} - C \log T \quad (18)$$

where  $A$  is an arbitrary constant.

Equation (18) is exactly analogous to the vapour pressure equation variously called Dupré's, Rankine's, and Kirchhoff's, but first deduced by the latter:

$$\log p = A - \frac{B}{T} - C \log T.$$

The name of Rankine might more appropriately be associated with the equation:

$$\log p = a - \frac{\beta}{T} - \frac{\gamma}{T^2} - \dots$$

(*Edin. Phil. Journ.*, 1849); the latter has recently been re-introduced, without any mention of Rankine, by E. Bose (*Physikal. Zeitsch.*, 1907, **8**, 944).

It is evident from the assumptions introduced in its deduction that equation (18) can, theoretically, be applied to dilute solutions only, just as Kirchhoff's equation should apply only to vapours at low pressures. Juliusburger (*Ann. Physik*, 1900, [iv], 3, 618) finds that the latter equation applies, in the case of some sixty liquids, not only at low temperatures and correspondingly small vapour pressures (when the saturated vapours may be assumed to conform to the gas laws), but also even as far as the critical point. He therefore considers that it may, in those regions where thermodynamic theory cannot guarantee any support, still be regarded as a remarkably exact interpolation formula with three parameters.

The authors have applied the equation (18) to the solubility data for some organic substances in organic solvents (Tyrer, *Trans.*, 1910, 97, 1778), and for sucrose in water (Landolt-Börnstein, *Tabellen*).

With the exception of one value in table III, the observed and calculated results agree to 0.7 per cent., and the differences are usually much less. This agreement is all the more remarkable when one considers that the more concentrated solutions—or rather syrups—contain as much as three parts by weight of sucrose to one of water, and cannot therefore be regarded in any way as "dilute." The analogy between solution and evaporation is here strikingly seen.

No assumptions have been made in the above argument as to the condition of the solute, and, as has been previously observed by one of us (Partington, *Trans.*, 1910, 97, 1158), such considerations are quite foreign to the spirit of the theory. In particular, equation (3) is not taken to imply any identity, or even physical similarity, between the state of the solute and that of a free gas. The real fundamental proposition of the thermodynamic theory of solution is contained in the assertion that the osmotic pressure of a solution, and every other property conditioned solely by it, depend simply on the number of solute molecules scattered through a given volume of solution, and not at all on the chemical nature of either solute or solvent, or on the relation between the latter, provided only that the solution is dilute. The chemical properties of solutions, on the contrary, depend, not only on the number, but also on the nature of the dispersed particles, and so are to a large extent conditioned by the exact mode of connexion between the solvent and solute.

It seems necessary to emphasise this point because of the fallacy, which unfortunately appears to be widely spread, that there is some fatal incompatibility between the old qualitative hydrate theory of solution and the new quantitative thermodynamic theory of which

ran't Hoff was the pioneer. This view has resulted from the one-sided outlook of the champions of each theory, and is certainly not a necessary consequence of the fundamental basis of either. It is greatly to be desired that writers on the theory of solution should distinguish clearly exactly which aspect of the subject belongs properly to their own investigations, and should refrain from attaching, on the basis of irrelevant experiments, a theory which is quite immune from the criticism which may reasonably be levelled against any particular hypothetical view of the nature of solutions.

The authors also find themselves unable to accept the statements of Tyrer (*loc. cit.*) to the effect that: "With non-associated solvents there is evidence for the belief that the solute (if it is not associated) does not associate with the solvent, but the molecules of both move freely among each other like the molecules of a mixed gas." Also: "In the majority of aqueous solutions, and in all cases where the solvent is an associated liquid, as, for example, a solvent containing a hydroxyl group, molecular association of the solvent and solute undoubtedly occurs, and the process of dissolution in these cases is probably due to these complex molecules." Apart from the use of "association" in more than one sense in this passage, it does not appear to render by any means obvious why two substances, which are not associated separately, should not combine when brought together, and certainly affords no reason why there should "undoubtedly" be combination if one substance happens to be associated.

The same author has introduced a magnitude which he calls the "concentration of the solvent," and defines as the number of grams of solvent in 1 c.c. of solution. The importance of this quantity appears, however, to have been over-estimated. The solubility of a substance is represented as a function of  $T$ , and the concentration of the solvent,  $C$ :

$$s = \phi(T, C).$$

[Tyrer's equation:

$$s = kf(T)\phi(C),$$

is an unnecessary divergence from standard mathematical usage.]

No new conception appears thereby to be introduced, as can be seen most simply if we remember that  $s$  and  $C$  are not independent, and that the equation therefore reduces to the well-known form:

$$s = f(T)$$

at constant pressure.

In the present paper it is shown that an expression for  $f(T)$  can be derived, which agrees with the experimental data.

If the pressure is not constant, an increase of pressure must, if the system is real, give rise to an increase of  $C$ , and therefore (since

# 1774. AN APPLICATION OF KIRCHHOFF'S EQUATION TO SOLUTIONS.

the solubility should increase with the latter unless very improbable properties of  $C$  are assumed) should invariably increase the solubility. This is by no means the case.

## EXPERIMENTAL.

All the solubilities are expressed in terms of the number of grams of solute per 100 grams of solvent in the saturated solution.

### (1) Anthraquinone in Benzene.

$$A = -44.369. \quad B = -805.111. \quad C = -16.6262.$$

Temp. abs.	Obs. s.	Calc. s.	Difference.
283	0.173	0.173	—
293	0.256	0.247	+0.009
303	0.350	0.350	0.000
313	0.495	0.495	—
323	0.700	0.695	+0.005
333	0.974	0.972	+0.002
343	1.355	1.355	—

### (2) Anthraquinone in Chloroform.

$$A = -2.479. \quad B = 748.8079. \quad C = -1.9516.$$

Temp. abs.	Obs. s.	Calc. s.	Difference.
283	0.457	0.457	—
293	0.605	0.602	-0.003
303	0.780	0.780	—
313	0.994	0.997	0.003
323	1.256	1.256	—
333	1.577	1.567	-0.010

### (3) Anthracene in Benzene.

$$A = -7.1236. \quad B = 1466.751. \quad C = 0.7960.$$

Temp. abs.	Obs. s.	Calc. s.	Difference.
283	0.975	0.975	—
293	1.43	1.425	-0.005
303	2.08	2.03	—
313	2.78	2.82	+0.04
323	3.75	3.84	+0.09
333	5.14	5.14	—
343	7.00	6.75	-0.25

### (4) Phenanthraquinone in Benzene.

$$A = -99.126. \quad B = 3450.512. \quad C = -35.3.$$

Temp. abs.	Obs. s.	Calc. s.	Difference.
283	0.412	0.412	$\pm 0.000$
293	0.536	0.538	—
303	0.730	0.719	-0.019
313	1.032	0.979	-0.053
323	1.354	1.354	—
333	1.760	1.89	+0.13
343	2.687	2.687	—
353	3.77	3.86	+0.09

(5) *Sucrose in Water.* $A = -32.235$ .  $B = -1283.65$ .  $C = -12.2267$ .

Temp. abs.	Obs. s.	Calc. s.	Difference.
273	179.2	179.2	—
288	190.5	189.8	- 0.7
293	203.9	203.2	- 0.7
303	219.5	219.5	—
313	238.1	239.8	+1.7
323	260.4	262.0	+1.6
333	287.3	288.4	+1.1
343	320.5	320.5	—

CHEMICAL DEPARTMENT,  
UNIVERSITY OF MANCHESTER.CC.—*The Action of Benzylamine on s-Dibromosuccinic Acid.*

By EDWARD PERCY FRANKLAND.

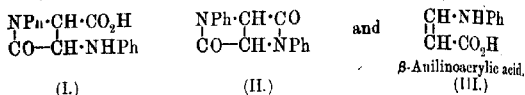
HITHERTO no experiments have been carried out on the action of aliphatic amines on symmetric dibromosuccinic acid, although the reaction with ammonia has been studied by several investigators with somewhat contradictory results. Thus Lindner and Lehrfeld (*Ber.*, 1881, **14**, 1816), acting on dibromosuccinic acid with alcoholic ammonia, obtained a small quantity of a diaminosuccinic acid decomposing at 200°, and practically insoluble in water, alcohol, or ether. This result was challenged by Claus (*Ber.*, 1882, **15**, 1849); who, working under the same conditions, obtained an almost theoretical yield of an intermediate product, namely, the ammonium salt of bromoaminosuccinic acid,  $\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}_2)\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$ , together with a minute quantity of ammonium diaminosuccinate. By the saponification of an ester prepared by the action of alcoholic ammonia on dibromosuccinic ethyl ester, Claus and Helpenstein (*Ber.*, 1881, **14**, 624) isolated a substance having the constitution of diaminosuccinic acid, but with properties differing from those of Lindner and Lehrfeld's acid; for example, this compound melted at 151°, and was soluble in water, alcohol, or ether. Lehrfeld showed, however (*Ber.*, 1881, **14**, 1816), that the action of alcoholic ammonia on dibromosuccinic ester gives rise, not to diaminosuccinic ester, but to iminosuccinamic ester,  $\text{NH} < \begin{smallmatrix} \text{CH}\cdot\text{CO}\cdot\text{NH}_2 \\ \text{CH}\cdot\text{CO}_2\text{Et} \end{smallmatrix}$ , a result confirmed by Hell and Poliakoff (*Ber.*, 1892, **25**, 640).

Lindner and Lehrfeld's diaminosuccinic acid was subsequently



prepared in larger quantity by Tafel (*Ber.*, 1887, **20**, 247; 1893, **26**, 1980) by the reduction of tartaric acid phenylhydrazone and osazone. In this case two isomeric acids were produced, one of which, apparently identical with Lindner and Lehrfeld's acid, yielded *i*-tartaric acid with nitrous acid, whereas the other, which was more soluble in water, acid, and alkali, and crystallised with one molecule of water, gave rise to racemic acid.

The action of aniline on dibromosuccinic acid has been studied<sup>1</sup> by Reissert (*Ber.*, 1893, **26**, 1758), who isolated three distinct substances, which he formulated as:



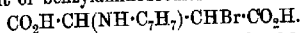
The first of these can be hydrolysed with sodium hydroxide to give a dianilinosuccinic acid, apparently identical with that prepared by Gorodetzki and Hell (*Ber.*, 1888, **21**, 1795) from dianilinosuccinic ethyl ester.

Reissert and Junghahn (*Ber.*, 1893, **26**, 1766) have shown that *p*-toluidine yields derivatives with dibromosuccinic acid exactly analogous to the anilino-derivatives mentioned above.

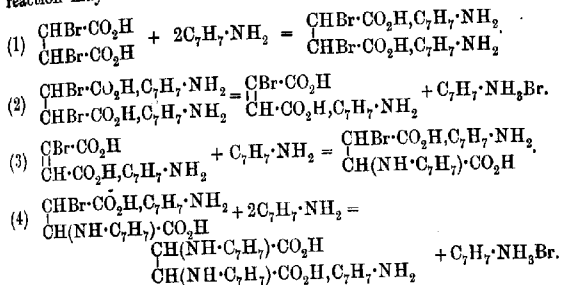
In examining the action of benzylamine on dibromosuccinic acid, the author has obtained different results according as the solvent used was water or alcohol. The course of the reaction can be followed more easily in the latter solvent, owing to the comparatively sparing solubility in alcohol of the various substances liable to be formed. The reaction proceeds, as might be expected, in a manner more analogous to the case of ammonia than to that of aniline, and bears a general resemblance to the reaction described by Claus (*Ber.*, 1882, **15**, 1849). A benzylaminobromosuccinic acid (benzylamine salt) appears during the early stages of the reaction, but is gradually converted into a dibenzylamino-acid, which in its properties closely resembles the diaminosuccinic acid described by Lehrfeld and by Tafel. The displacement of the second bromine atom by a benzylamino-group thus proceeds with much greater ease than in the case of the amino-group. Whereas Lehrfeld obtained only 4 grams of diaminosuccinic acid from 200 grams of dibromosuccinic acid, the author was able to prepare 7.2 grams of dibenzylaminosuccinic acid (monobenzylamine salt) from 8 grams of dibromosuccinic acid, corresponding with a yield of 57 per cent.

On mixing alcoholic solutions of benzylamine and dibromosuccinic acid, the dibenzylamine salt of dibromosuccinic acid separated in the course of a few minutes. When this substance was recrystallised from alcohol, it underwent a change, losing hydrogen bromide, and

yielding presumably the monobenzylamine salt of bromomaleic acid. If the reaction mixture, which contained 4 molecules of amine to one of acid, was heated on the water-bath, another product was deposited; this was found to consist of two distinct substances, one melting at 156—157°, the other decomposing at 232°. The substance of low melting point was found, on analysis, to be the monobenzylamine salt of benzylaminobromosuccinic acid,



Both this substance and the benzylamine salt of bromomaleic acid are stable when heated with alcohol, but are slowly converted into the substance decomposing at 232° when a few drops of benzylamine are added to the boiling solution. On analysis, this substance appeared to be the monobenzylamine salt of dibenzylaminosuccinic acid,  $\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}\cdot\text{C}_7\text{H}_7)\cdot\text{CH}(\text{NH}\cdot\text{C}_7\text{H}_7)\cdot\text{CO}_2\text{H}$ . The course of the reaction may be illustrated by the following equations:



The first equation represents the formation of a precipitate of the dibenzylamine salt of dibromosuccinic acid, which, in the second equation, is converted into the monobenzylamine salt of bromomaleic acid. The third equation shows the probable method of formation of the monobenzylamine salt of benzylaminobromosuccinic acid, a substance which also has a transitory existence in the reaction mixture when heated on the water-bath under reflux, passing into the final product, the monobenzylamine salt of dibenzylaminosuccinic acid as shown in the fourth equation.

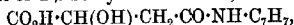
The free acid can be obtained from the crude benzylamine salt by dissolving the latter in concentrated hydrochloric acid and precipitating with water. Benzylamine hydrochloride remains in the aqueous solution, and the yield of free acid from the amine salt corresponds with theory.

When benzylamine was allowed to react on dibromosuccinic acid in aqueous solution, two products were obtained, one of which was soluble in ammonia, and proved, on analysis, to be the dibenzyl-

amine salt of dibenzylaminosuccinic acid, the other, insoluble in ammonia and melting at 203–207°, gave, on analysis, figures indicating the formula  $C_{18}H_{20}O_4N_2$ . This substance possessed properties quite unlike those of the isomeric dibenzylaminosuccinic acid, and it was found to be identical with the dibenzylamide of *i*-tartaric acid prepared by the author by heating together benzylamine and *i*-tartaric acid. The dibenzylamide of racemic acid was also prepared; it melted at practically the same temperature as the *i*-compound, but gave a considerable lowering of the melting point when mixed with the product obtained from dibromosuccinic acid. Apparently the formation of a tartramide derivative from *i*-dibromosuccinic acid is not accompanied by a Walden inversion, as otherwise we should expect a benzylamide of racemic acid to be produced.

The only dibenzylamide of tartaric acid known hitherto was prepared by P. Frankland and Slaton (Trans., 1903, **83**, 1362) from methyl *d*-tartrate. It is described as crystallising in white, glistening plates, soluble in alcohol, insoluble in water, and melting at 199°.

Lutz (Diss., Rostock; Abstr., 1901, i, 7) has shown that both ammonia and benzylamine react on monohalogen succinic acids to form monoamides of malic acid instead of the expected aspartic acids. Thus, *l*-monobromosuccinic acid with benzylamine yields the benzylamine salt of *d*- $\beta$ -benzylmalamic acid,



presumably owing to migration of oxygen from the carboxyl group to the  $\beta$ -position during the removal of bromine as benzylamine hydrobromide. An analogous reaction in the case of dibromosuccinic acid would lead to the dibenzylamide of a tartaric acid; most probably *i*-tartaric acid, since *s*-dibromosuccinic acid yields principally a diaminosuccinic acid, which, according to Tafel, is converted by nitrous acid into *i*-tartaric acid.

#### EXPERIMENTAL.

##### I.—Action of Benzylamine on Dibromosuccinic Acid in Ethyl-Alcoholic Solution.

(a) A solution of 6.2 grams of dibromosuccinic acid in 70 c.c. of absolute ethyl alcohol was treated with 10 grams of benzylamine. The solution became warm, and a crystalline precipitate was thrown down. This was collected and washed with alcohol and ether; after drying in the steam-oven, it weighed 10.4 grams. Theory requires 11.0 grams of the dibenzylamine salt of dibromosuccinic acid. The substance crystallised in well-defined prisms, and melted without charring at 149°. It contained no ionic bromine:

\* All temperatures here given are uncorrected.

0.1029 gave 82.81 c.c.  $\text{CO}_2$  and 4.91 c.c.  $\text{N}_2$ .  $\text{C}=43.87$ ;  $\text{N}=5.66$ .

0.2497 „ 0.1919  $\text{AgBr}$ .  $\text{Br}=32.70$ .

$\text{C}_{10}\text{H}_8\text{O}_4\text{N}_2\text{Br}_2$  requires  $\text{C}=44.08$ ;  $\text{N}=5.71$ ;  $\text{Br}=32.65$  per cent.

A portion of the substance was dissolved in absolute alcohol. After some time, the solution deposited large, broad, prismatic plates and needles, which melted at  $145^\circ$ . The mother liquor contained ionic bromine. This substance, the *monobenzylamine* salt of *bromomaleic acid*, dissolved readily in water and in alcohol, and the aqueous solution decolorised permanganate instantly in the cold:

0.1036 gave 83.35 c.c.  $\text{CO}_2$  and 3.97 c.c.  $\text{N}_2$ .  $\text{C}=43.75$ ;  $\text{N}=4.82$ .

0.1255 „ 101.75 c.c.  $\text{CO}_2$  „ 4.63 c.c.  $\text{N}_2$ .  $\text{C}=43.65$ ;  $\text{N}=4.63$ .

$\text{C}_{11}\text{H}_{11}\text{O}_4\text{NBr}$  requires  $\text{C}=43.71$ ;  $\text{N}=4.64$  per cent.

When a small quantity of the substance was heated in alcoholic solution with a few drops of benzylamine for about half an hour on the water-bath, a precipitate began to form. After about one hour's heating, the precipitate was collected, and washed with alcohol and ether. It decomposed at  $236^\circ$ . After dissolving in concentrated hydrochloric acid and precipitating with water, the substance decomposed at  $251^\circ$ , and crystallised from aqueous ammonia in stellate aggregates of prisms (*dibenzylaminosuccinic acid*). The acid mother liquor yielded crystals of benzylamine hydrochloride (m. p.  $253^\circ$ ).

(b) A solution of 5 grams of dibromosuccinic acid in 70 c.c. of absolute alcohol was treated with 8 grams of benzylamine. On heating on the water-bath, the precipitate formed on mixing dissolved, and after about fifteen minutes another precipitate began to deposit. The solution was then cooled, the precipitate collected, and washed with alcohol and ether. After drying in the steam-oven, it weighed 5.9 grams. A specimen melted and decomposed at  $180^\circ$ , and contained no ionic bromine. The substance was boiled with absolute alcohol, the insoluble portion collected and washed with hot alcohol, and finally with ether. After drying in the steam-oven, this portion weighed 1.15 grams. It decomposed at  $232^\circ$  [compare experiment (c)]. On cooling the alcoholic solution and washings, a crystalline substance separated out. It was washed with a little alcohol and with ether, and after drying weighed 2.22 grams. This substance contained no ionic bromine; it crystallised in rectangular plates, melting at  $156$ – $157^\circ$ , which were readily soluble in water, but sparingly so in cold alcohol; the aqueous solution did not decolorise permanganate in the cold. Most

\* (Carbon and nitrogen combustion in a vacuum.) All gas volumes are corrected to N.T.P.

probably this substance is the *monobenzylamine salt* of *benzylaminobromosuccinic acid*:

0.0893 gave 87.47 c.c.  $\text{CO}_2$  and 5.00 c.c.  $\text{N}_2$ . C=52.64; N=7.04.

0.2724 „ 0.1237 AgBr. Br=19.32.

$\text{C}_{18}\text{H}_{20}\text{O}_4\text{N}_2\text{Br}$  requires C=52.81; N=6.85; Br=19.56 per cent.

This substance apparently could not be converted into dibenzylaminosuccinic acid by boiling with alcohol, but on adding a drop of benzylamine and heating for three-quarters of an hour on the water-bath, a white precipitate was formed similar to that appearing in the reaction mixture of benzylamine and dibromosuccinic acid on continued heating. It decomposed at  $242^\circ$ , and crystallised from aqueous ammonia in the groups of prismatic crystals characteristic of dibenzylaminosuccinic acid.

(c) A solution of 5 grams of dibromosuccinic acid in 70 c.c. of absolute alcohol was heated to boiling with 8 grams of benzylamine. The precipitate formed was collected from time to time, washed with hot alcohol, and the washings returned to the mother liquor. In this way, the more soluble benzylaminobromosuccinic acid (benzylamine salt) was submitted to the continued action of alcoholic benzylamine. The first fraction, collected after one hour's heating, weighed 2.85 grams, and decomposed at  $238^\circ$ . The second fraction, collected after another hour's heating, weighed 1.13 grams, and decomposed at  $242^\circ$ .

The mother liquor was finally evaporated to dryness, and the residue dissolved in water. A quantity of benzylamine hydrobromide passed into solution, and the insoluble portion was collected and washed with alcohol, whereby some brown, tarry matter was removed. The total weight of insoluble product obtained from this experiment was 4.9 grams. Theory requires 7.9 grams of the *monobenzylamine salt* of *dibenzylaminosuccinic acid*:

0.0704 gave 89.46 c.c.  $\text{CO}_2$  and 5.53 c.c.  $\text{N}_2$ . C=68.45; N=9.88.

0.0884 „ 6.91 c.c.  $\text{N}_2$ . N=9.82.

$\text{C}_{25}\text{H}_{20}\text{O}_4\text{N}_3$  requires C=68.96; N=9.65 per cent.

This substance was very sparingly soluble in water or alcohol, readily so in concentrated acids and in aqueous ammonia. Both acids and ammonia removed benzylamine from the molecule, and from the hydrochloric acid mother liquor, crystalline plates of benzylamine hydrochloride (m. p.  $254^\circ$ ) could be isolated. The substance crystallising out from acid on dilution, or from ammonia on concentration, was dibenzylaminosuccinic acid. From the latter solvent it appeared in small, spherical aggregates of acicular prisms, which decomposed at  $251^\circ$ . Some specimens, even after repeated recrystallisation, decomposed at as low a temperature as  $249^\circ$ , others not below  $253^\circ$ .

Four grams of the benzylamine salt of dibenzylaminosuccinic acid were dissolved in concentrated hydrochloric acid, the solution was diluted with a large volume of water, and the resulting precipitate collected, washed with water, alcohol and ether, and dried. It weighed 3 grams. Theory requires 3 grams of *dibenzylaminosuccinic acid*.

The substance was practically insoluble in water, alcohol, or ether, but, like its benzylamine salt, was readily dissolved by concentrated acids and by aqueous ammonia:

0.0801 (dec. 253°) gave 97.61 c.c. CO<sub>2</sub> and 5.49 c.c. N<sub>2</sub>. C=65.43; N=8.62.

0.0847 (dec. 250—251°) gave 102.84 c.c. CO<sub>2</sub> and 5.84 c.c. N<sub>2</sub>. C=65.56; N=8.66.

C<sub>18</sub>H<sub>20</sub>O<sub>4</sub>N<sub>2</sub> requires C=65.86; N=8.54 per cent.

The solution of this substance in a small volume of concentrated hydrochloric acid occasionally solidified to a crystalline mass which did not redissolve on adding excess of acid, but passed into solution in warm water. The aqueous solution almost instantly deposited the free dibenzylaminosuccinic acid. The substance separating from the acid solution was collected, and freed from hydrochloric acid by washing with ether, and finally by keeping in a vacuum over soda-lime and sulphuric acid. It melted and decomposed at 165°, and gave, on analysis, figures indicating approximately the composition of a *dihydrochloride of dibenzylaminosuccinic acid*:

0.2022 gave 0.1402 AgCl. Cl=17.16.

0.2063 „ 0.1430 AgCl. Cl=17.15.

C<sub>18</sub>H<sub>20</sub>O<sub>4</sub>N<sub>2</sub>.2HCl requires Cl=17.71 per cent.

## II.—Action of Benzylamine on Dibromosuccinic Acid in Aqueous Solution.

A solution of 8 grams of dibromosuccinic acid in 100 c.c. of water was treated with 12.4 grams of benzylamine (six molecules). The solution became warm. It was heated to boiling under reflux, and became cloudy after about ten minutes. After about half an hour's heating, a yellow, tarry product appeared, and a precipitate of small, glancing plates was deposited. The heating was continued, and a white, flocculent precipitate appeared in addition to the plates. The solution was filtered hot after one and a-half hours' heating, and the product washed with water, alcohol, and ether. It weighed 2.7 grams, and decomposed at 212°. The filtrate was heated for two and a-quarter hours longer, when a second fraction was obtained, weighing 1.7 grams, and decomposing at 225°. Another hour's heating yielded only 0.15 gram of product.

The products thus obtained were warmed with aqueous ammonia. The precipitate of small plates remained undissolved, and was collected, washed with water, with alcohol to remove tar, and finally with ether. After drying, it weighed 0.85 gram. The substance had a pale green tinge, and melted at 203°. After recrystallisation from a large volume of alcohol, it appeared in small, colourless, rhomboidal plates, melting at 203—207°, practically insoluble in water, sparingly soluble in alcohol, insoluble in ammonia, and only slowly dissolved by hot concentrated hydrochloric acid. Two other experiments, one with 3.8 grams, the other with 5 grams of dibromosuccinic acid, with 4 molecules of amine, yielded 0.6 and 0.7 gram respectively of this substance, the *dibenzylamide* of tartaric acid:

0.0814 gave 99.46 c.c. CO<sub>2</sub> and 5.59 c.c. N<sub>2</sub>. C=65.78; N=8.62.

0.1916 „ 0.4610 CO<sub>2</sub> and 0.1100 H<sub>2</sub>O. C=65.63; H=6.38.

C<sub>18</sub>H<sub>20</sub>O<sub>4</sub>N<sub>2</sub> requires C=65.86; H=6.10; N=8.54 per cent.

A portion of this substance was dissolved by prolonged boiling with concentrated hydrochloric acid, and the solution was evaporated to a syrup and stirred with alcohol. A precipitate of crystalline plates was collected and recrystallised from alcohol. On examination, this substance was shown to be benzylamine hydrochloride. It melted at 253°, and contained ionic chlorine. (Found, C=58.79; N=9.79. Calc., C=58.54; N=9.76 per cent.)

In order to compare the product melting at 203—207° with the *dibenzylamides* of *i*-tartaric and racemic acids respectively, these substances were synthesised by heating together the respective acids with benzylamine (2 molecules) for seven and a-half and nine and a-half hours at 130° to 150°. The resulting products were purified by repeated recrystallisation from alcohol.

The *dibenzylamide* of *i*-tartaric acid crystallised from alcohol in small, rhomboidal plates, which melted at 203—205°:

0.0838 gave 102.42 c.c. CO<sub>2</sub> and 5.86 c.c. N<sub>2</sub>. C=65.83; N=8.78.

C<sub>18</sub>H<sub>20</sub>O<sub>4</sub>N<sub>2</sub> requires C=65.86; N=8.54 per cent.

A mixture of this substance with the product obtained from dibromosuccinic acid melted at 203—207°.

The *dibenzylamide* of racemic acid crystallised from alcohol in rhomboidal plates, similar to the above, which melted at 206—207°:

0.0842 gave 102.45 c.c. CO<sub>2</sub> and 5.85 c.c. N<sub>2</sub>. C=65.55; N=8.72.

C<sub>18</sub>H<sub>20</sub>O<sub>4</sub>N<sub>2</sub> requires C=65.86; N=8.54 per cent.

A mixture of this substance with the product obtained from dibromosuccinic acid melted at 192—195°.

Hence the product from dibromosuccinic acid is the *dibenzylamide* of *i*-tartaric acid, not of racemic acid.

It was observed that the *dibenzylamide* of *i*-tartaric acid, whether

prepared from tartaric acid or from dibromosuccinic acid, was coloured yellow on melting, whereas the dibenzylamide of racemic acid remained practically colourless.

The ammoniacal extract of the reaction product from benzylamine and dibromosuccinic acid was concentrated to a small bulk, whereupon a substance separated out, which decomposed at  $221^{\circ}$ . After two recrystallisations from hydrochloric acid and water a product was obtained, decomposing at  $250^{\circ}$ , and having the characteristic appearance of dibenzylaminosuccinic acid.

In another experiment the product crystallising out after the tartramide derivative had been removed was recrystallised from hot water containing a few drops of benzylamine. The substance dissolved only sparingly in hot water alone, but the solubility was much greater than that of the monobenzylamine salt of the dibenzylamino-acid obtained in alcoholic solution. It separated from the aqueous benzylamine solution in prisms, which melted and decomposed at  $226-227^{\circ}$ . On analysis this substance proved to be the dibenzylamine salt of *dibenzylaminosuccinic acid*:

0.0797 gave  $104.46$  c.c.  $\text{CO}_2$  and  $6.56$  c.c.  $\text{N}_2$ .  $\text{C}=70.58$ ;  $\text{N}=10.35$ .

$\text{C}_{32}\text{H}_{38}\text{O}_4\text{N}_4$  requires  $\text{C}=70.85$ ;  $\text{N}=10.31$  per cent.

In another experiment the above product, after filtration from the reaction mixture, was treated with boiling aqueous alcohol. The greater part passed into solution, leaving a small residue of white, crystalline substance, decomposing at  $232^{\circ}$ . On analysis this compound was shown to have the composition of free dibenzylaminosuccinic acid. (Found,  $\text{C}=65.65$ ;  $\text{N}=8.75$ . Calc.,  $\text{C}=65.86$ ;  $\text{N}=8.54$  per cent.)

CHEMICAL DEPARTMENT,  
THE UNIVERSITY, EDGBASTON, BIRMINGHAM.

## CCl.—A Method of Determining Carbon and Nitrogen in Organic Compounds.

By EDWARD PERCY FRANKLAND.

THE Frankland-Armstrong vacuum combustion process (*Journ. Chem. Soc.*, 1868, **21**, 77), originally designed for the determination of minute quantities of carbon and nitrogen in water analysis, can be adapted for the determination of carbon and nitrogen in organic compounds without having recourse to the usual apparatus for gas analysis. This method is in use in a very few chemical laboratories.



for the estimation of nitrogen, but, so far as the author is aware, it has not been customary to collect and measure the carbon dioxide evolved, and thus by means of a single combustion to determine both nitrogen and carbon.

Besides the Sprengel pump, the only apparatus necessary is a couple of glass measuring tubes graduated in tenths of a c.c., one of about 150 c.c. capacity, the other 50 c.c. or less, together with glass cylinders, in which the tubes may be levelled over mercury and water respectively.

The operation can be performed in considerably less time than that required for an ordinary carbon-hydrogen combustion; only one weighing is necessary (that of the substance taken for combustion), and satisfactory results can be obtained by the combustion of 0.1 gram of substance and even less.

The figures obtained by this method for a variety of organic substances containing nitrogen are generally more accurate than the average of figures obtained by the ordinary carbon-hydrogen combustion process. The method is of special utility in the case of a preliminary analysis of a substance of unknown constitution, figures for carbon and nitrogen being generally of greater value in fixing a formula than those for carbon and hydrogen. The results obtained by this method of analysis are not affected by the presence of halogens, a substance containing over 80 per cent. of bromine yielding very nearly theoretical figures for nitrogen and carbon; hence this process appears to be of especial advantage in connexion with substances containing both nitrogen and halogen.

The substance to be analysed is mixed with fine copper oxide, and introduced into a combustion tube (closed at one end), which is then filled with the usual length of coarse copper oxide. A reduced copper spiral is fitted in, and the tube is then drawn out before the blow-pipe, attached to the Sprengel pump, and exhausted. During the last stages of the exhaustion some burners are lighted below the copper spiral. The combustion is carried out in the ordinary manner, and the gas evolved is collected over mercury in a glass vessel graduated in tenths of a c.c., closed by a tap at one end. When the gas has ceased to pass over, the combustion tube is thoroughly exhausted with the pump, and the measuring vessel transferred to a cylinder of mercury in a room free from draughts. The temperature is registered by a sensitive thermometer hanging beside the glass vessel, and the volume of gas at atmospheric pressure is read off through a telescope. This measurement gives the volume of moist carbon dioxide and nitrogen.

The gas is now treated with strong aqueous potassium hydroxide introduced through a bent pipette to absorb carbon dioxide, and

when the liquid has remained at the same level for ten minutes with occasional shaking, it is allowed to diffuse out into water recently boiled to free it from dissolved air. The residual gas (nitrogen) is then expelled through the glass tap (by sinking the measuring vessel in a cylinder of water) into a narrow glass measuring tube graduated in tenths of a c.c. This is necessary, as it was found convenient to have the upper portion of the large measuring vessel ungraduated and expanded to take a large volume of gas, thus reducing the length of the apparatus.

The nitrogen gas is finally measured over water, and the weights of nitrogen and of carbon dioxide determined by reference to density tables.

Below are given the details of a combustion of  $\beta$ - $\gamma$ -dibromopropylamine hydrobromide:

0.3129 gave 104.5 c.c.  $\text{CO}_2 + \text{N}_2$  at  $16.8^\circ$  and 647 mm. Volume of  $\text{N}_2$  after absorption with  $\text{KOH}$  = 12.8 c.c. at  $16.8^\circ$  and 756 mm.  $\text{C} = 12.08$ ;  $\text{N} = 4.73$ .

$\text{C}_3\text{H}_5\text{NBr}_2$  requires  $\text{C} = 12.08$ ;  $\text{N} = 4.70$  per cent.

The results of other combustions carried out by this method will be found in the preceding paper.

CHEMICAL DEPARTMENT,  
THE UNIVERSITY, EDGBASTON, BIRMINGHAM.

## CCII. — *The Absorption Spectra of the Isomeric Hydrazones and Semicarbazones of Camphorquinone.*

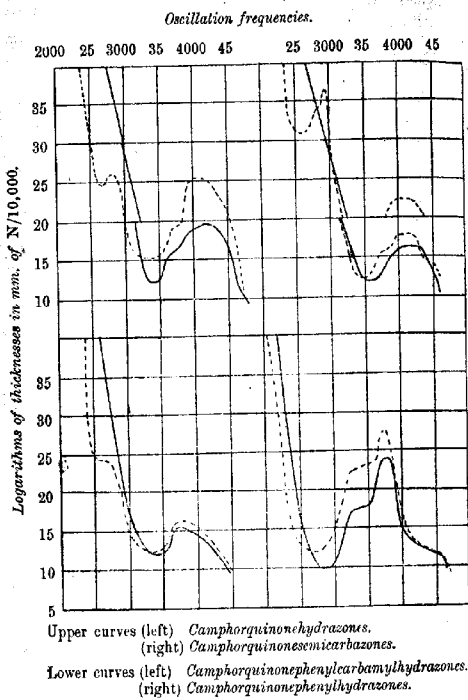
By FREDERICK RUSSELL LANKSHEAR and ARTHUR LAPWORTH.

FORSTER and Zimmerli have recently shown that the products obtained by the condensation of camphorquinone with hydrazine, semicarbazide, phenylcarbamyldiazide, and phenylhydrazine can exist in two isomeric forms in each case (Trans., 1910, **97**, 2156; this vol., 478). The properties of the compounds appeared to point unmistakably to the conclusion that both forms must be regarded as conventional hydrazones with azethenoid linkings, and consequently the existence of stereoisomerism in the sense of the Hantzsch-Werner hypothesis was inferred.

Certain definite characteristics of the members of each pair led Forster and Zimmerli to classify one of each as an  $\alpha$ -derivative and the other as a  $\beta$ -derivative, a similar spacial relationship being

supposed to subsist between the four representatives of each class respectively.

We are much indebted to Dr. Forster, who kindly gave us the opportunity of comparing the absorption spectra of these eight compounds, and our results are shown in the appended figures. As usual, the depths of the solution varied from 10 mm. to 100 mm.



The full curves refer to the  $\alpha$ -modifications and the others to the  $\beta$ -modifications.

and in each case three solutions,  $N/100$ ,  $N/1000$ , and  $N/10,000$  respectively, were examined.

Each of the  $\beta$ -representatives, except in the case of the phenylhydrazone, shows an irregularity at 2600—2700, which in the case of the hydrazone develops to a shallow band with its head at 2718, and in that of the semicarbazone to a moderately deep one with its head at 2950. There is no sign of such irregularities in the case

the corresponding compounds. The  $\beta$ -series, moreover, are uniformly less transparent to the longer wave-lengths (below 2700—3400), but more transparent to wave-lengths shorter than these, and the persistence is invariably somewhat greater than in the  $\alpha$ -series. Apart from these points there is a general resemblance between the spectra of the two members of each pair, and the principal bands have their heads comparatively near one another, at 2800—3600. It should be added that the absorption spectrum of the  $\alpha$ -phenylhydrazone has already been examined by Baly, Luck, Marsden, and Gazdar (*Trans.*, 1907, **91**, 1572), the curve of which corresponds closely with that shown above, except that the short and nearly horizontal portion at 3200—3500 in the above diagram is seen in the earlier figure as a shallow band.

The absorption spectra of the camphorquinone derivatives exhibit conspicuous deviations from Beer's law, and this is most marked in the case of the  $\beta$ -semicarbazone, as the diagram shows sufficiently clearly.

It seems almost beyond question that the  $\alpha$ -compounds form one series, and the  $\beta$ -compounds another, as was inferred by Forster and Zimmerli, the general relations of the pairs being of much the same character throughout; it appears highly probable that whatever is the nature of the isomerism between the members of one pair, the same explanation must be given for each of the other three pairs. It would be premature in our present state of knowledge of the relationship between chemical constitution and absorption spectra to suggest that the spectroscopic results throw any light on the nature of the isomerism, but there is nothing which tends to weaken the case made out by Forster and Zimmerli in favour of the application of the Hantzsch-Werner hypothesis to the case. The close general resemblance between the ultraviolet absorption spectra of the phenylhydrazones in particular is a most striking feature, and would probably cause surprise if the isomers were known to be structurally different, for example, in the sense that one represented a hydrazone and the other an azo-compound.

The spectra were photographed with the aid of a spectrograph made by Hilger, and kindly presented to the Chemical Department of this University by Mr. C. A. Schunck. The authors also desire to express their indebtedness to Professor E. C. C. Baly, who presented the plates used in calibrating the photographs, and offered many valuable suggestions.

CHEMICAL LABORATORIES,  
THE UNIVERSITY, MANCHESTER.

CCHIL.—*The Solubility of Cuprous Oxide in Aqueous Ammonia Solutions, and the Composition of the Cuprous-ammonia Complex.*

By FREDERICK GEORGE DONNAN and JOHN SMEATH THOMAS.

In the following paper an account is given of determinations of the solubility at 25° of crystalline cuprous oxide in aqueous ammonia solutions of varying strengths. The investigation was primarily undertaken in order to throw some light, if possible, on the composition of the cuprous-ammonia complexes existing in such solutions.

*Preparation of Materials.*

The cuprous oxide was prepared as follows. Equal weights of copper sulphate and sucrose were dissolved in water, and potassium hydroxide solution added until almost the whole of the precipitate had re-dissolved. This solution was kept at 70° until the cuprous oxide had separated out. Two batches of oxide were prepared in this way. In the first case the solution was large in bulk and relatively dilute, the cuprous oxide separating slowly and possessing a dark red colour, whilst in the second case, when the solution was much more concentrated, the precipitate formed in a shorter time, and was bright red. This second preparation proved to be slightly more soluble in ammonia solutions than the first. This is probably due to the fact that it consisted of smaller crystals.

In each case the oxide was collected by the aid of the pump, well washed with water, then with alcohol and ether, and dried in a vacuum desiccator over sulphuric acid. Analysis of these preparations gave: *Preparation I* (dark red), Cu = 88.62. *Preparation II* (bright red), Cu = 88.59.  $\text{Cu}_2\text{O}$  requires Cu = 88.68 per cent.

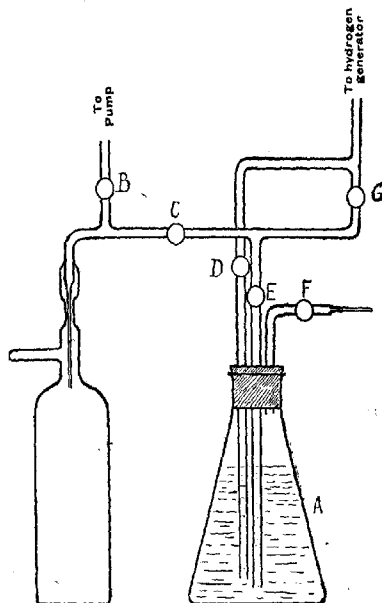
The stock ammonia solution was prepared by distilling ordinary "pure" concentrated ammonia solution over lime, the gas being passed into pure distilled water. The concentrated stock solution so prepared was carefully guarded from entrance of carbon dioxide, and was diluted as required.

*Apparatus and Method.*

The apparatus used for the solubility determinations is shown in the accompanying figure. It consists essentially of a narrow-necked bottle, with a device for introducing the ammonia solution and sealing in an atmosphere of hydrogen. The bottle has a long, narrow neck, which, after the solid has been introduced, is con-

stricted. A tube, one end of which has been drawn out to a capillary, is passed through the constriction and then sealed, first of all into the neck of the bottle (inside seal), and then to the rest of the apparatus.

The ammonia solution is contained in the flask *A*, and as a preliminary, air is removed from this and the flask by a stream of hydrogen which escapes through *F*. The process of filling the



bottle with ammonia solution was as follows. The bottle is first exhausted, and then filled with hydrogen by closing *B* and opening *C* and *G*. This was repeated several times to ensure the removal of all air, after which the bottle was finally exhausted. On now opening *C*, *E*, and *D* (keeping *B*, *G*, and *F* closed), the air-free ammonia solution is driven over by the pressure of the hydrogen into the bottle, the capillary delivery tube preventing any wetting of the constriction. As soon as sufficient solution has been driven over, *E* is closed, and the remaining space in the bottle filled with

hydrogen at nearly atmospheric pressure by opening the taps. Finally, after the taps are closed, the bottle immersed in ice (to reduce the ammonia pressure), and the constricted neck of the bottle sealed up without removing the inside capillary tube. It was found quite possible to do this, if the capillary tube was sufficiently thin. A little finely divided copper was generally added to the solid cuprous oxide to remove any trace of oxygen remaining in the bottle, and to reduce any small quantity of cupric oxide accidentally present. Special experiments showed that a small excess of metallic copper had no effect on the solubility of the cuprous oxide, as might be expected. The sealed bottles containing the cuprous oxide (in excess) and ammonia solution were rotated in a thermostat at 25° for periods varying from a fortnight to a month. A careful series of preliminary determinations had shown that equilibrium was attained in a fortnight.

#### *Method of Analysis.*

After equilibrium was attained, the bottles were removed from the rotating shaft, and allowed to remain in a vertical position in the thermostat for a week. If the experiment had been successfully carried out up to this point, the solution was quite clear and colourless. Any bottles the contents of which showed the slightest trace of a bluish tinge (indicating slight oxidation) were rejected.

The solution was removed for analysis as follows. The side-tube of the bottle was first opened, and rapidly connected to a hydrogen generator. The neck was then cut, and a cork carrying a pipette at once inserted. The lower end of the pipette was kept at least an inch from the solid at the bottom of the bottle. The clear solution was now quietly forced up into the pipette by the pressure of the hydrogen, whereupon the contents of the pipette were without delay run into a weighed flask containing a weighed amount (in excess) of dilute sulphuric acid. The top portion of the contents of the pipette was rejected, in order to guard against loss of ammonia during the process of filling the pipette.

The total ammonia was estimated by distilling over from excess of alkali in the usual way. In the remaining liquid the excess of alkali was neutralised by nitric acid, the solution then made considerably acid by more nitric acid, and the copper deposited electrolytically on a rotating platinum cathode (platinum crucible). The deposited copper was washed, dried, and weighed with the usual precautions.

*Experimental Results.*

In tables I and II are given the results of the solubility determinations at 25°, with the two preparations of cuprous oxide previously referred to.

TABLE I.

*Preparation No. 1.*

Concentration of total copper.		Concentration of total ammonia.	
Grams per 1000 grams of solution.	Mols. per 1000 grams of solution.	Grams per 1000 grams of solution.	Mols. per 1000 grams of solution.
0.3593	0.00536	3.91	0.23
0.5024	0.00791	12.07	0.71
0.8369	0.01080	13.77	0.81
0.8964	0.01095	16.15	0.95
1.0144	0.01597	27.03	1.59
1.0482	0.01645	32.64	1.92
1.0557	0.01660	36.89	2.17
1.2243	0.01924	45.73	2.69
1.3229	0.02081	68.68	4.04
1.4882	0.02340	74.12	4.26
1.5105	0.02375	81.26	4.78
1.6313	0.02565	98.52	5.56
1.6981	0.02670	122.40	7.20

TABLE II.

*Preparation No. 2.*

Concentration of total copper.		Concentration of total ammonia.	
Grams per 1000 grams of solution.	Mols. per 1000 grams of solution.	Grams per 1000 grams of solution.	Mols. per 1000 grams of solution.
0.4229	0.00665	7.82	0.46
0.6678	0.01050	8.16	0.48
0.9890	0.01555	22.61	1.33
1.0494	0.01650	28.39	1.67
1.3528	0.02127	54.15	3.19
1.5047	0.02366	72.08	4.24
1.5963	0.02510	78.20	4.60
1.6555	0.02603	102.05	6.00

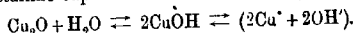
A comparison of curves plotted from the results given in tables I and II shows that Preparation No. 2 is uniformly more soluble than Preparation No. 1. As stated before, this is probably due to the fact that No. 2 contains a much larger proportion of very small, micro-crystalline particles.

*Formula of the Cuprous-Ammonia Complex.*

Owing to the excessively small solubility of cuprous oxide in pure water, the solutions obtained in the foregoing experiments must contain practically only a complex cuprous-ammonia hydroxide, the formula of which we may represent as  $(\text{Cu} \cdot n\text{NH}_3)\text{OH}$ , and the



corresponding ions. The solution may in reality contain a number of different complex hydroxides, corresponding with different values of  $n$ , in which case the value of  $n$  obtained in the following calculation will represent an average value. We shall proceed, however, on the simplifying assumption that the solutions contain in the main only one type of complex, and endeavour to ascertain the corresponding value of  $n$  (compare Bonsdorff, *Zeitsch. anorg. Chem.*, 1904, 41, 132). The condition of saturation with respect to solid, crystalline cuprous oxide leads to the equilibria:

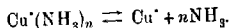


For dilute solutions we may therefore write:

$$[\text{Cu}^*] \times [\text{OH}'] = L \dots \dots \dots (1).$$

where  $L$  is a constant.\* It may be observed that this relation can only be an approximation, and perhaps a very rough approximation, for the stronger ammonia solutions, since, quite apart from the "physical" effect of the increasing ammonia concentration on the solubility of cuprous oxide, the quantity  $L$  involves the concentration of the water in the solution.

The dissociation of the complex ion  $\text{Cu}^*(\text{NH}_3)_n$  leads to the equilibrium:



The concentration of ammonia, as ammonium hydroxide and "free" ammonia, will be equal to  $[\text{NH}_3] - n[\text{Cu}]$ , where  $[\text{NH}_3]$  = molar concentration of total ammonia, and  $[\text{Cu}]$  = molar concentration of total copper.

In not too strong solutions, since  $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH}$ , we may put the concentration of "free" ammonia as approximately proportional to  $[\text{NH}_3] - n[\text{Cu}]$ .

The dissociation-equilibrium of the complex cuprous-ammonia kation leads then to the equation:

$$[\text{Cu}^*] \times \{[\text{NH}_3] - n[\text{Cu}]\}^n = k[\text{Cu}^*(\text{NH}_3)_n] \dots \dots (2).$$

Elimination of  $[\text{Cu}^*]$  between equations (1) and (2) leads to the equation:

$$\frac{[\text{Cu}^*(\text{NH}_3)_n] \times [\text{OH}']}{\{[\text{NH}_3] - n[\text{Cu}]\}^n} = \frac{L}{k} \dots \dots \dots (3).$$

As the copper will exist in the solution practically only as complex hydroxide, and as this, owing to its small concentration, may be regarded as nearly completely ionised, we may without great error write  $[\text{Cu}^*(\text{NH}_3)_n] = [\text{Cu}]$ .

If, further, we neglect the concentration of  $\text{OH}'$ -ion due to

\* In this equation and the following equations the square brackets indicate molar concentrations.

ionisation of ammonium hyroxide in comparison with that arising from the complex hydroxide, we may write also:

$$[\text{OH}'] = [\text{Cu}(\text{NH}_3)_n] = [\text{Cu}].$$

It may be observed here that this last approximation requires justification (see later, p. 1795). With these approximations, equation (3) assumes the form:

$$\frac{[\text{Cu}]^2}{[\text{NH}_3] - n[\text{Cu}]} = \frac{L}{k} = \text{const.} \quad (4).$$

Since the analytical results give directly the values of  $[\text{Cu}]$  and  $[\text{NH}_3]$ , equation (4) may be employed to determine the value of  $n$ .

For example, if  $n=2$ , then  $\frac{[\text{Cu}]}{[\text{NH}_3] - 2[\text{Cu}]} = \text{constant}$ .

If we put the concentration of free ammonia in the solution proportional to the partial pressure ( $p_{\text{NH}_3}$ ) of ammonia in the vapour-phase in equilibrium with the solution, we can write (4) in the form:

$$\frac{[\text{Cu}]^2}{p_{\text{NH}_3}} = \text{const.} \quad (5).$$

The values of  $p_{\text{NH}_3}$  were obtained from the results of Perman at 25° (Trans., 1901, 79, 718; 1903, 83, 1168), allowance being made in each case for the ammonia combined with the copper.

In the following table are shown the results as calculated from the solubility-data of table I. The values of  $[\text{Cu}]$  and  $[\text{NH}_3]$  have been read from a smooth curve drawn from these data.

TABLE III.

$[\text{Cu}]$	$[\text{NH}_3]$	$\frac{[\text{Cu}]^2}{[\text{NH}_3] - [\text{Cu}]}$ $k_1$	$\frac{[\text{Cu}]^2}{p_{\text{NH}_3}}$ $k_2$	$\frac{[\text{Cu}]^2}{[\text{NH}_3] - 2[\text{Cu}]}$ $k_3$
0.0050	0.28	$91 \times 10^{-6}$	$71 \times 10^{-4}$	$185 \times 10^{-4}$
0.0090	0.60	$137 \times 10^{-6}$	$104 \times 10^{-4}$	$157 \times 10^{-4}$
0.0130	1.20	$142 \times 10^{-6}$	$105 \times 10^{-4}$	$111 \times 10^{-4}$
0.0170	2.04	$138 \times 10^{-6}$	$104 \times 10^{-4}$	$85 \times 10^{-4}$
0.0210	3.36	$132 \times 10^{-6}$	$92 \times 10^{-4}$	$63 \times 10^{-4}$

Although both  $k_1$  and  $k_2$  exhibit an undoubted maximum, the relative constancy of these values in comparison with the wide variation of  $k_3$  points unmistakably to the value  $n=1$ , and the formula  $(\text{Cu} \cdot \text{NH}_3)\text{OH}$  for the complex cuprous-ammonia hydroxide.

It may be remarked that the values given under  $[\text{Cu}]$  and  $[\text{NH}_3]$  are expressed in terms of mols. per 1000 grams of solution, and not in terms of mols. per litre. The varying density of the ammonia solutions will therefore to some extent affect the constancy of  $k_1$  and  $k_2$  ( $k_3$  will clearly not be affected). As the variation in density of the ammonia solution does not amount to more than two or three per cent., this source of error may be neglected for the

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 purposes of the present calculation. In order to obviate an  
 objection, the following table shows the values of  $\frac{[\text{Cu}]^2}{[\text{NH}_3] - [\text{Cu}]}$   
 where both  $[\text{Cu}]$  and  $[\text{NH}_3]$  are expressed as fractional molar co-  
 ncentrations; for example:

$$[\text{Cu}] = \frac{\text{Mols. copper}}{\text{Mols. copper} + \text{mols. ammonia} + \text{mols. water}}$$

TABLE IV.

Values of  $k_1$  for fractional molar concentrations.

$16.3 \times 10^{-7}$
$24.7 \times 10^{-7}$
$25.8 \times 10^{-7}$
$25.1 \times 10^{-7}$
$21.5 \times 10^{-7}$

These values correspond in order with the values given in table  
 III, and exhibit a similar maximum.

As shown in table II, the second preparation of cuprous oxide  
 showed uniformly higher solubilities in ammonia solution than the  
 first preparation. The following table (V) shows the values of  $k_1$   
 as calculated from the solubility data given in table II. The values  
 of  $[\text{Cu}]$  and  $[\text{NH}_3]$  have been, as in the previous case, read from  
 a smooth curve drawn through the experimental points.

TABLE V.

$[\text{Cu}]$	$[\text{NH}_3]$	$\frac{[\text{Cu}]^2}{[\text{NH}_3] - [\text{Cu}]}$
0.005	0.220	$116 \times 10^{-6}$
0.009	0.505	$163 \times 10^{-6}$
0.0130	0.970	$176 \times 10^{-6}$
0.0170	1.710	$171 \times 10^{-6}$
0.0210	2.990	$149 \times 10^{-6}$

As pointed out previously, in arriving at the equation whereby  
 the values of the "constants" have been calculated, the ionisation  
 of ammonium hydroxide in presence of the highly dissociated  
 cuprous-ammonia hydroxide was neglected. How far such an  
 approximation is justifiable may be seen from the following con-  
 siderations.

Let  $c$  = molar concentration of total ammonia.

$pc$  = molar concentration of total copper.

Assuming the copper all present in the solution as  $\text{Cu}(\text{NH}_3)_2\text{OH}$ ,  
 and this as practically completely ionised, the hydroxyl ion concen-

ation corresponding therewith will be  $pc$ . If  $\alpha$  = degree of ionisation, and  $k$  = ionisation constant of ammonium hydroxide,\* then:

$$k(1-p)(1-\alpha)c = (1-p)\alpha c \times \{(1-p)\alpha + p\}c, \\ k(1-\alpha) = \alpha c \{(1-p)\alpha + p\}.$$

In this equation  $p$  and  $c$  are known from the analytical data, and the values of  $k$  can be obtained from the data of Goldschmidt (*Zeitsch. anorg. Chem.*, 1901, 28, 122). Hence,  $\alpha$  can be calculated, and so the values of  $(1-p)\alpha c$  (hydroxyl ion concentration due to ammonia) determined and compared with the values of  $pc$  (hydroxyl ion concentration due to cuprous ammonia hydroxide). The results of this calculation are shown in the following table.

TABLE VI.

[NH <sub>3</sub> ].	[Cu].	[OH'] in pure ammonia solution.	[OH'] due to ammonia in cuprous ammonia solution.	[OH'] due to cuprous ammonia hydroxide.
0.28	0.0050	0.0098	0.00093	0.0050
0.60	0.0090	0.0072	0.0011	0.0090
1.20	0.0130	0.0048	0.0013	0.0130
2.04	0.017	0.0036	0.0013	0.0170

Table VI shows that in the solutions investigated the hydroxyl ion concentration arising from the ionisation of the uncombined ammonia is, in the stronger ammonia solutions, sufficiently small in comparison with that due to the ionisation of the cuprous ammonia hydroxide (assumed practically completely ionised). The approximation introduced into the main calculation (see p. 1793) is therefore justified in the case of not too dilute solutions of ammonia, as the following table shows.

TABLE VII.

[Cu].	[NH <sub>3</sub> ].	$k_1 = \frac{[Cu][OH']}{[NH_3] - [Cu]}$
0.005	0.28	$108 \times 10^{-6}$
0.009	0.60	$154 \times 10^{-6}$
0.013	1.20	$156 \times 10^{-6}$
0.017	2.04	$154 \times 10^{-6}$

In the above table  $[OH']$  = molar concentration of total hydroxyl ion, as calculated from the results given in table VI.

These considerations suffice to explain the rise of the "constant" in the more dilute solutions of ammonia. The fall observed in the stronger ammonia solutions is almost certainly to be ascribed to the "salting-out" effect of the ammonia, and the decrease in the concentration of the water, both of which will tend to diminish the

\*  $\alpha$  is really the "apparent" degree of ionisation, and  $k$  the "pseudo" ionisation constant, of the total uncombined ammonia.

quantity  $L$ , the "solubility-product" of the cuprous oxide (compare p. 1792). Dawson, in his investigation of the solubility of crystalline cupric hydroxide in aqueous ammonia solutions (*Zeitsch. physikal. Chem.*, 1909, **69**, 114), has observed a similar variation of the analogous "constant" (where, however,  $n=4$ ). Our explanation of the variation is substantially the same as that given by Dawson, with whom we entirely agree.

It is curious that we find the formula  $(\text{Cu}^{\text{I}}\cdot\text{NH}_3)\text{OH}$  for the complex cuprous ammonia hydroxide, whereas Dawson's results are best explained by the formula  $(\text{Cu}^{\text{II}}\cdot 4\text{NH}_3)(\text{OH})_2$ . Bonsdorf (*loc. cit.*) deduced from his work on the solubility of cupric hydroxide in ammonia solution the formula  $(\text{Cu}^{\text{II}}\cdot 2\text{NH}_3)(\text{OH})_2$  but Dawson has conclusively demonstrated the erroneous nature of this result; thus, when the copper atom changes as regards its primary positive valency from the univalent to the bivalent state, its secondary or residual valency, that is, combining capacity, for ammonia increases in a greater proportion. The composition of many complex cuprous and cupric compounds (containing a complex copper cation) supports this conclusion (compare Abegg's *Handbuch der anorg. Chem.*, II, 1, p. 536).

THE MUSPRATT LABORATORY OF PHYSICAL AND ELECTRO-CHEMISTRY,  
THE UNIVERSITY OF LIVERPOOL.

#### CCIV.—*The Synthesis of Hydrocarbons at High Temperatures.*

By JOHN NORMAN PRING and DORIAN MACEFIELD FAIRLIE.

IN a previous investigation by one of us (*Trans.*, 1910, **97**, 489) the synthesis of methane was investigated between the temperatures  $1200^\circ$  and  $1500^\circ$ . The yield of methane diminished somewhat with progressive use of the same carbon, but finally attained a constant value. This decrease in the methane formation was probably due to graphitisation of the carbon, the minimum values being obtained from the first when graphite was used.

The formation of ethylene was observed at  $1800^\circ$  and at higher temperatures. In experiments carried out at  $1200^\circ$ — $1500^\circ$ , the final quantity of methane obtained appeared to be increased by using platinum as a catalyst in contact with the carbon. No satisfactory explanation could be given of this, nor of the fact that the amount of methane, which, of course, diminishes with the temperature,

egan to increase at  $1550^{\circ}$ , although the formation of acetylene could not be detected below about  $1800^{\circ}$ .

The points which still remain to be cleared up are whether the quantities of methane obtained in these earlier experiments between  $200^{\circ}$  and  $1500^{\circ}$  are the true equilibrium values, or is the yield affected by the intermediate formation of traces of acetylene or some other hydrocarbon which it has not yet been found possible to detect, or is it affected by any other cause.

Gautier and Clausmann (*Compt. rend.*, 1910, 151, 355) have shown that by the action of oxides of iron on mixtures of carbon monoxide and dioxide at  $1250^{\circ}$ , an amount of methane is formed which is equal to 0.20 per cent. of the hydrogen present. This is probably a rough measure of the equilibrium value, but the conditions of the experiment were not sufficiently precise for an exact evaluation.

In order to elucidate the remaining points of uncertainty, the following series of experiments were carried out in the present research.

*Part I.*—The influence of different catalysts on the final quantity of methane obtained.

*Part II.*—The surrounding of the heated carbon rod by an electric field of high potential in order to influence any ionisation effect from the heated carbon.

*Part III.*—The detection of any hydrocarbons formed in very small quantity, or as intermediate compounds, by rapid continuous circulation of the gas through the apparatus, and then through charcoal, cooled by liquid air, in order to condense and retain any hydrocarbons as soon as possible after their formation.

*Part IV.*—Measurements were made of the rate at which acetylene and ethylene react with hydrogen at different temperatures, and the nature of the products obtained was ascertained.

#### *Part I.—Effect of Catalysts.*

The form of apparatus used was the same as that described in the earlier work (*Trans.*, 1910, 97, 500). The hydrogen was purified by filtering through a palladium tube (*loc. cit.*, p. 502). The only part of the apparatus to be subjected to a high temperature was the carbon. Temperature readings were made, as before, by means of the Wanner optical pyrometer, which was first carefully calibrated.

*Analysis of Gas.*—In the samples in which acetylene was absent, the gas was withdrawn from the apparatus, stored over glycerol and water, and analysed by taking from 1000 to 1500 c.c. and

removing the excess of hydrogen with palladium foil, until the volume was reduced to 35–50 c.c.

After removal of the carbon monoxide, a fractional combustion of the hydrogen was brought about by mixing the gas with an excess of oxygen, and passing through a U-tube containing palladium black, and maintained at 80–100° in a small water-bath (compare Hempel, *Gas Analysis*, 1906, p. 178). After complete removal of the hydrogen in this way, the remaining mixture was ignited by a spark, and the contraction measured. The carbon dioxide formed was then removed by potassium hydroxide. By noticing the ratio between the contraction after ignition and the carbon dioxide formed, the saturated hydrocarbon was always identified as methane, for which the above ratio was always found to be 2:1 (with ethane this would be  $2\frac{1}{2}$ :2, and with propane 1:1).

For a satisfactory analysis of the gases obtained in experiments where unsaturated hydrocarbons were present, it was found necessary to make an examination of the methods available for the separation of acetylene and ethylene.

*Use of Ammoniacal Silver Nitrate.*—By taking a mixture of acetylene and hydrogen it was found that, provided the reagent was fresh, the whole of the former was absorbed by a concentrated solution of ammoniacal silver nitrate, after shaking for three minutes.

35.5 C.c. of pure ethylene were shaken with the same reagent. The absorption after three minutes amounted to 7.63 c.c., and after another three minutes' treatment a further 2.5 c.c. was absorbed.

Bromine water containing an excess of bromine was found completely to absorb acetylene and ethylene, if shaken, after three minutes. No means of absorbing acetylene without affecting the ethylene was found. Ammoniacal silver nitrate was used, with which the absorption of the acetylene was complete, and that of the ethylene assumed to amount to one-quarter to one-fifth of the total quantity present. The remainder of the ethylene was absorbed by treating the gas with bromine water, followed by potassium hydroxide solution. The hydrogen and methane were then estimated as described above.

*Purification of Carbon.*—The carbon, in the form of a rod, usually 4 mm. in diameter and about 8 cm. long, was purified by heating in chlorine to about 1400° for one to two hours in a vessel similar to the reaction vessel, but in which the brass water-cooled holders were previously coated with shellac. This form of apparatus is specially suited for this purification, as the chlorides formed from the impurities distil rapidly away, and condense in the cold parts of the apparatus. The vessel was always evacuated, and refilled with

chlorine several times while the heating was continued. The carbon was then heated in hydrogen in the same manner for the same time, the apparatus being frequently exhausted to a low pressure. After transferring to the reaction vessel (*loc. cit.*, p. 501), the carbon was heated for two to three hours, to about  $1200^{\circ}$ , at the low pressure of about 0.01 mm. In this way, the ash content of the carbon was usually reduced to below 0.1 per cent., and the hydrogen below 0.01 per cent. In the case of the carbon rods which were used in presence of platinum or palladium as a catalyst, these metals, to the amount of about 0.2 gram, were coated on the carbon, by electrodeposition, after the treatment in chlorine. The order of the experiments has been carefully noted in the results below to show in some cases the effect of continued use of the same carbon.

*Use of Platinum as a Catalyst.*

Carbon coated with Platinum. 4 mm.  $\times$  11 cm.

Order of experiment.	Duration.	Temp. (approx.)*	Product.	
			CO.	CH <sub>4</sub> . Per cent.
1.	1½ hrs.	1250°	0.09	0.522
2.	3½ „	1150	0.11	0.702

Carbon coated with Palladium. No. 1. 5 mm.  $\times$  11.2 cm.

1.	1½ hrs.	1175°	0.08	0.630
2.	½ hr.	1400	0.22	0.328

Carbon coated with Palladium. No. 2. 5 mm.  $\times$  5.5 cm.

1.	1½ hrs.	1320°	0.08	0.498
2.	3 „	1450	0.56	0.212

*Carbon coated with Silicon.*—The rod (5 mm.  $\times$  9 cm.) was coated with an even deposit of silicon by heating in an atmosphere of hydrogen and silicon tetrachloride, at about  $1700^{\circ}$ , for twenty minutes under conditions which have been determined by one of us, in conjunction with W. Fielding (*Trans.*, 1909, 95, 1497).

Order of experiment.	Duration.	Temp. (approx.)*	Product.			
			CO.	CH <sub>4</sub> . Per cent.	C <sub>2</sub> H <sub>6</sub> .	C <sub>2</sub> H <sub>4</sub> .
1.	1½ hrs.	1225°	0.004	0.218	—	—
2.	1 hr.	1600	0.56	0.286	0.0016†	—
3.	35 mins.	1710	0.02	0.467	0.95	†

The above results show that there is no appreciable difference between platinum and palladium in their influence as catalysts in assisting the reaction, and that silicon has no appreciable catalytic effect. The results obtained with platinum are in complete agreement with those found in the earlier work (*loc. cit.*, p. 510).

\* Not corrected for departure from "black body" radiation from the coated surface.

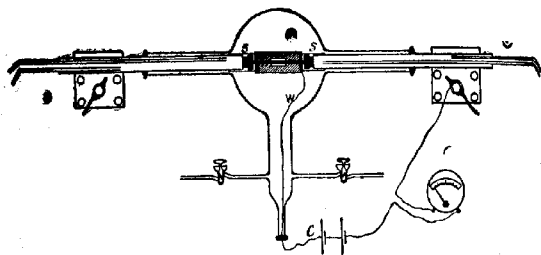
† Estimated colorimetrically.



*Part II.—Influence of an Electric Field Surrounding the Heated Carbon.*

At the suggestion of Mr. R. E. Slade, a number of experiments were carried out to ascertain if any influence is exerted by ionisation from the carbon on the formation of methane. A cylinder of fine platinum gauze, 8 cm. long and 2 cm. in diameter, was taken (Fig. 1). A rectangular opening in the middle 1 cm.  $\times$  0.6 cm. was made to allow an uninterrupted view of the rod by the pyrometer. Thin tubes of fused silica were inserted at *SS* to prevent contact of the platinum with the brass tubes. A wire at *W* enabled electrical contact to be made with the cylinder *S*. The whole of this was then mounted in the reaction vessel by sliding through the side-tubes, and the wire *W* allowed to emerge through

FIG. 1.



the neck at the bottom, where an air-tight joint was made by means of wax. In this way, a difference of potential could be applied between the heated rod and the surrounding cylinder by means of a circuit *C*, which is independent of the one used for heating the rod. A difference of potential of from 200 to 400 volts in either direction could thus be maintained, and the ionisation current measured by using a milliammeter in the circuit.

With a carbon rod 9 cm. long and 5 mm. in diameter, heated in an atmosphere of hydrogen, the following values were found for the ionisation current:

Temp.	Ionisation current when field on gauze was	
	+ 200 to 300 milliams.	- 200 to - 300 milliams.
1200°	0.02	—
1550	0.88	0.07
1625	1.20	0.08
1720	—	0.11
1845	5.0	—

The current produced when the platinum was negatively charged must have arisen from the negative ionisation of this metal, which became heated by radiation from the carbon, as subsequent work on the ionisation from carbon at high temperatures has shown that no measurable amount of positive ions are produced at any temperature below 2000°.

*Rod No. 1.*—Amorphous carbon, 9 cm. × 5 mm., purified as described above (p. 1800.)

Order of experiment.	Duration.	Temp.	Charge on platinum cylinder.	Product.			
				CO.	CH <sub>4</sub> . Per cent.	C <sub>2</sub> H <sub>2</sub> .	C <sub>2</sub> H <sub>4</sub> .
1.	3 hrs.	1330°	+210	0.5	0.212	—	—
2.	2½ „	1330	-375	0.14	0.200	—	—
3.	1 hr.	1560	+360	0.62	0.260	—	—

*Rod No. 2.*—Partly purified by heating in a high vacuum for three hours at 1200°.

1.	8 mins.	1850°	+210	1.6	1.46	0.43	0.90
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The rod was afterwards analysed, and found to contain 0.32 per cent. of ash.

*Rod No. 3.*—Partly purified by heating electrically in chlorine for fifteen minutes at about 1200°, and then in hydrogen, and, after mounting in reaction vessel, heating in a high vacuum for four hours to about 1200°.

1.	12 mins.	1850°	-200	2.5	1.01	0.60	0.50
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*Rod No. 4.*—Not purified. 5 mm. × 8 cm.

1.	12 mins.	1850°	+210	2.1	0.57	0.40	0.32
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*Rod No. 5.*—Not purified. 4 mm. × 8 cm.

1.	7½ mins.	1825°	-220	5.0	0.69	0.50	?
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*Rod No. 6.*—4 mm. × 7 cm. Purified by heating in chlorine for fifteen minutes, then in hydrogen for the same time, and finally in a vacuum for an hour.

1.	5 mins.	1900°	+220	4.2	0.50	1.05	?
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*Rod No. 7.*—5 mm. × 7 cm. Purified by heating electrically in hydrogen at 1600—1700° for three hours with occasional exhaustions.

Order of experiment.	Duration.	Temp.	Charge on platinum cylinder.	Product.			
				CO.	CH <sub>4</sub> Per cent.	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>
1.	30 mins.	1560°	-200	0.24	0.248	—	—
2.	30 "	1680	-200	0.50	—	trace (0.001%)	—
3.	30 "	1650	+200	0.05	0.220	trace (0.001%)	—
4.	30 "	1550	+200	<0.005	0.180	—	—
5.	30 "	1580	-190	<0.003	0.182	—	—
6.	70 "	1525	-195	<0.003	0.180	—	—
7.	3½ hrs.	1215	-220	<0.003	0.188	—	—
8.	3 "	1230	+340	0.01	0.201	—	—

At the end of this series the carbon rod was analysed, and found to contain 0.05 per cent. of ash.

The formation of acetylene at 1650° and 1680° was detected by passing a large quantity of the gas through a small washing spiral containing ammoniacal cuprous chloride, by which method the presence of 0.001 per cent. of acetylene can be shown. In this way it was possible to detect the acetylene formed at a temperature about 100° below that previously found.

The above experiments, in which long-continued use was made of the same carbon, show clearly that ionisation by the carbon makes no difference to the yield of methane. The quantity of methane obtained at 1525—1550°, namely, 0.180 per cent., is in agreement with the results obtained in earlier work (Trans., 1910, 97, 510).

At the lower temperatures, 1215—1330°, where the reaction has been found to be so slow, sufficient time was not allowed for the formation of methane to reach its maximum value, but the above experiments prove that the ionisation of carbon has no effect on the rate at which methane is formed.

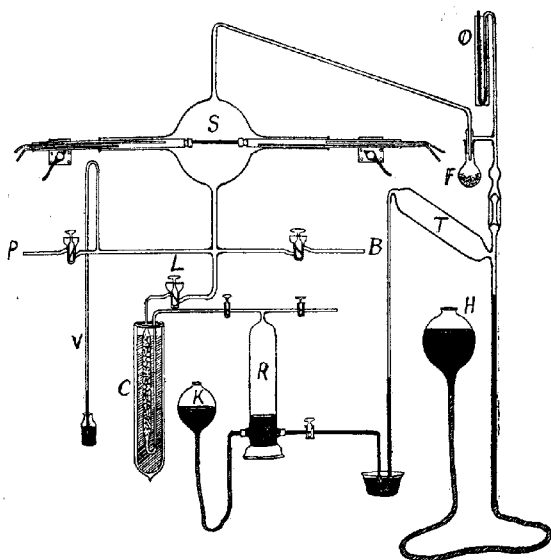
*Part III.—Detection of Hydrocarbons formed as Intermediate Compounds, or in very small quantities, by continuously circulating the gas through the reaction vessel at different pressures, and then at atmospheric pressure through charcoal at -180°.*

The reaction vessel was similar to the one previously used, but of smaller capacity. The globe *S* (Fig. 2) was 13 cm., and the side-tubes 1.3 cm. in diameter. The water-cooled brass tubes fitting into these were 1 cm. in diameter. Graphite plugs were inserted in the sealed brass tubes as usual, and an amorphous carbon rod of 3 or 4 mm. diameter and 7 to 8 cm. long was fitted.

The pressure of gas inside the apparatus was indicated by the mercury gauge *V* and the vacuum gauge *O*. The vessel was exhausted to a fraction of a millimetre by means of a Sprengel automatic mercury pump connected to *P*. The vessel was filled with pure hydrogen, which entered at *B*, after passing through a

ated palladium tube. The large Töpler pump *T*, fitted with a drying bulb *F*, enabled gas to be quickly removed from the reaction vessel at any pressure, and passed into the reservoir *B*, where, by regulating the height of the mercury *K*, the pressure was usually adjusted to be a little above atmospheric. By then turning and carefully regulating the tap *L*, the hydrogen could be slowly re-admitted into the reaction vessel, after passing through the tube *C* containing coconut charcoal, which was kept immersed in liquid air. It was, of course, first necessary to saturate the charcoal with

FIG. 2.



hydrogen, a large quantity of which is absorbed at atmospheric pressure. A very rapid circulation of gas and removal of absorbable constituents could thus be carried out at different gaseous pressures in *S*. However, since this absorption is probably not complete, the method cannot be applied for precise quantitative results.

In many of the experiments, the operation of the Töpler pump was made mechanical by the use of a motor and pulley for raising and lowering the reservoir *H*. In this way a steady and known rate of circulation could be kept up for several hours.

*Fractional Separation of Hydrocarbons by Absorption with Charcoal at Low Temperatures.*

It was found that if methane and acetylene, together with a large excess of hydrogen, are absorbed in charcoal cooled by liquid air ( $-190^{\circ}$  to  $-180^{\circ}$ ), and if the liquid air is then replaced by a mixture of ether and carbon dioxide ( $-80^{\circ}$ ) and the gas withdrawn from the charcoal until the pressure is reduced to 3 mm., then nearly all the hydrogen is given off, about one-third of the methane (b. p.  $-160^{\circ}$ ), and only a trace of the acetylene (b. p.  $-85^{\circ}$ ). On removing the ether and carbon dioxide, the remaining gases, consisting of hydrogen, methane, acetylene, ethylene, carbon monoxide, and dioxide, could then be removed by the Sprengel pump. The last traces of acetylene and ethylene could only be removed, however, by warming the charcoal for some time in a high vacuum.

*Reaction between Unsaturated Hydrocarbons and Hydrogen when Absorbed in Charcoal.*

It is well known that charcoal, by condensing, has the power of bringing about reactions between gases which do not take place under ordinary conditions, and it became consequently necessary to ascertain if any influence of this kind is exerted on acetylene or ethylene when in presence of hydrogen.

In the use of charcoal for dealing with gaseous carbon compounds, an obstacle which is encountered is due to the difficulty of entirely removing such compounds as carbon dioxide, water vapour, and other readily condensable gases from the charcoal, small quantities of such gases constantly reappearing during future use of the charcoal. The charcoal used in these experiments was prepared by carefully carbonising cocoanut shell, which was then granulated, and a small quantity placed in a glass tube. This was exhausted for four or five days with a Sprengel pump, and the charcoal heated from time to time with a Bunsen flame. Hydrogen was then admitted several times, in some cases after cooling the charcoal by liquid air, and then pumped off until a high vacuum was obtained. After treating in this manner, some hydrogen was admitted, withdrawn after warming the charcoal, and, on analysis, still found to contain 1 c.c. of carbon dioxide.

A number of experiments were carried out, in which mixtures of acetylene or ethylene and hydrogen were left in contact with cocoanut charcoal at different temperatures. The reaction between these unsaturated hydrocarbons and oxygen was investigated in a similar manner. The results showed that the reaction between acetylene and hydrogen, when occluded in charcoal and heated at

100–200°, leads to the formation of ethylene in quantities not exceeding about 2 per cent., and an amount of methane which is smaller than this.

In presence of oxygen, acetylene and ethylene are partly oxidised at about 200°, but only slightly, if at all, at room temperatures. Exact measurements of the amount of carbon dioxide present when only in small quantities was prevented by the difficulty of completely removing this gas from the charcoal after each experiment. The results show that carefully purified cocoanut charcoal can, without appreciable error, be used for the fractional separation of hydrocarbons in presence of hydrogen.

After these preliminary experiments, use was made of the circulation apparatus described above, and shown in Fig. 2. If the intermediate formation of acetylene or any other stable hydrocarbon takes any part in the yield of methane, then by continuously circulating the gases through the reaction vessel and through the cold charcoal tube, any such compounds will be partly or entirely condensed, and after a sufficient quantity has collected, can be removed and analysed in the usual manner.

Experiments were, in this way, carried out at various pressures. If acetylene plays any part in the reaction, it follows that by working at a lower pressure the ratio of the less condensed molecule acetylene to the more condensed methane will be higher than at a higher pressure. The pressure of gas in the reservoir *R* (Fig. 2) and in the charcoal was usually higher than atmospheric, to enable more efficient condensation, and to obviate leaks through the rubber stoppers at the base of the reservoir.

*Purification of Charcoal.*—In order to remove the last traces of acetylene from the freshly prepared charcoal, it was found necessary to exhaust to the lowest possible pressure for a period of several days, occasionally heating and admitting hydrogen. It is probably not at all possible to remove all the water vapour and denser hydrocarbons. After the purification treatment, none of the latter were evolved, however, with the gases during subsequent experiments, so that their presence did not interfere with the measurements.

In the experiments of this series, very particular precautions were taken to obtain the carbon in the purest condition. In addition to the usual preliminary purification, only carbon was taken which had been used for a long interval in previous experiments, where it had undergone prolonged heating in hydrogen.

The experiment below is described in some detail, as it is typical of the remainder in this series.

*Expt. 1.*—The carbon rod (7 cm.  $\times$  4 mm.), which had been coated with platinum, was heated for five and a-half hours at 1400° in

hydro\_ a pressure of 12 to 14 cm. The pressure of gas in the mercury reservoir (*Z*) was kept at 74 cm. (in all subsequent experiments this was kept at 77 cm.). The speed of circulation of the gas was arranged so that the volume in the vessel was renewed every two minutes. The total volume of gas circulated through the charcoal and measured at N.T.P. was estimated at 38 litres. A quantity of hydrogen was then removed from the charcoal while still at  $-180^{\circ}$ , until the pressure was reduced to 2 cm. The liquid air around the charcoal was then replaced by ether and carbon dioxide at  $-80^{\circ}$ , and 720 c.c. of gas removed, which reduced the pressure to about 1 cm. Most of the hydrogen was removed from this gas by condensing with palladium foil, and the residue found to contain 6.23 c.c. of methane and 2.10 c.c. of carbon monoxide. After warming the tube to room temperature, 22.5 c.c. more gas were withdrawn (the last portions being obtained by warming to about  $200^{\circ}$ ). This last sample was found to contain 1.15 c.c. of ethylene, 0.72 c.c. of carbon monoxide, and 3.95 c.c. of methane, and no other hydrocarbon. The total gas condensed therefore contained:

$\text{CH}_4$ , 10.18 c.c., or 0.026 per cent. of whole.

$\text{C}_2\text{H}_4$ , 1.15 c.c., " 0.003 " "

$\text{CO}$ , 2.85 c.c., " 0.007 " "

The experiments in this series can be represented in tabular form as follows:

No. of experiment.	Temp. of carbon.	Pressure of gas (cm.).	Duration of experiment.	Total volume of gas circulated (litres N.T.P.).	Percentage composition of gas.			
					$\text{CH}_4$ .	$\text{C}_2\text{H}_4$ .	$\text{C}_2\text{H}_2$ .	$\text{CO}$ .
4.	1200°	7-30	4 hrs.	26	0.049	0.0005	nil.	0.01
2.	1225	50-60	10½ "	80	0.010	0.00014	nil.	0.04
1.	1400	12-14	5½ "	38	0.026	0.003	nil.	—
3.	1400	10-25	9 "	31	0.039	0.002	nil.	—
5.	1650	7-30	1½ "	10	0.1104	0.0025	0.012	—
6.	1800	76	7 mins.	2.5	—	0.052	0.024	0.11

Experiments 2 and 6 were conducted with pure carbon, and the others with platinum coated rods. In Nos. 3 to 5, the same carbon rod was used.

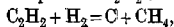
*Blank Experiments.*—Experiments were made to ascertain the extent to which impurities in any part of the apparatus, such as vapours from tap grease or wax, might have contributed to the hydrocarbon formation in any of the present work. For this purpose, use was made of a platinum strip, instead of carbon, and a complete experiment carried through, as in part III above, and another as in part I. It was found in both cases that the amount of methane was less than 5 per cent. of that obtained when using carbon under the same conditions.

*Part IV.—Rate of Reaction of Acetylene and Ethylene with Hydrogen, and rate of Decomposition of Methane at various temperatures.*

In the present work, which extends some preliminary measurements already made by one of us (Trans., 1910, 97, 508), a simple means was devised to follow continuously the course of the reaction between acetylene and hydrogen, and the measurements were extended to the reaction between ethylene and hydrogen. The rate of decomposition of the methane formed into carbon and hydrogen could also be observed.

*Apparatus.*—A porcelain tube of 2 cm. internal diameter and 60 cm. long was arranged inside an electrical wire resistance furnace, so that the tube could be heated to any temperature up to 1200°, which could be read by means of a thermocouple placed alongside. The tube was provided with a manometer, and gases could be introduced at one end and removed at the other by means of a Töpler pump, whereby the tube could be exhausted.

A mixture of the hydrocarbon and hydrogen could be admitted, and in virtue of the volume change, the reaction could be followed by the change of pressure indicated by the manometer. Accurate measurements could thus be made of the relative rates of the formation of methane from hydrogen and acetylene, or ethylene, and of its decomposition; thus, in the case of acetylene and hydrogen reacting according to the equation  $C_2H_2 + 3H_2 = 2CH_4$ , or



the methane formed is, in either case, equal to the contraction. When all this methane is decomposed, the volume will again assume its original value. It was found that this second change, the decomposition of methane, was very slow compared with the first, so that the first could be measured independently of the second without appreciable error.

The acetylene used was prepared from calcium carbide, and, after washing through concentrated potassium hydroxide solution, was liquefied by liquid air, redistilled, and then collected over a heavy oil in a gas-holder. A sample of the gas was analysed, and found to contain 95.5 per cent. of acetylene. This and another holder filled with hydrogen were placed in connexion with the porcelain tube, and, after exhausting, either gas could be admitted to the heated tube and the volume ascertained by reading the manometer.

The temperature of the tube was kept constant to within about 10° throughout the experiment.

The pressure at first was always atmospheric, and the course of the reaction could be followed by the rise of mercury in the manometer.



meter. After a definite period, the remaining gas was removed and submitted to analysis.

*Expt. 1.*—Temperature  $720^{\circ}$ .  $C_2H_2=21$ ;  $H_2=79$ .\*

Time (mins.) .....	0	5	8	13	16	18	21
Pressure (mm.) .....	760	717	702	688	677	672	668

Final composition of gas,  $C_2H_2=9.5$ ;  $C_2H_4=2.0$ ;  $CH_4=10.0$ .  
Contraction= $12$  per cent.

*Expt. 2.*—Temperature  $980^{\circ}$ .  $C_2H_2=26.7$ ;  $H_2=73.3$ .

Time (mins.) .....	0	1	2	3	6	17	28	36	40
Pressure (mm.) ...	760	733	725	718	703	682	682	683	683.5

Final composition of gas,  $C_2H_2=3.08$ ;  $C_2H_4=0.56$ ;  $CH_4=11.9$ ;  
 $CO=2.9$ . Contraction= $10.1$  per cent.

*Expt. 3.*—Temperature  $745^{\circ}$ .  $C_2H_2=24.8$ ;  $H_2=75.2$ .

Time (mins.) .....	0	1	3	6	10	16	25	40	143	183	188	233
Pressure (mm.) ...	760	747	730	714	697	680	662	648	612	610	610	607

Final composition,  $C_2H_2=1.91$ ;  $C_2H_4=1.0$ ;  $CH_4=16.9$ ;  $CO=0.8$ .  
Contraction= $20$  per cent.

No other hydrocarbons but the above were found in any of these experiments.

*Reaction between Ethylene and Hydrogen.*—This was investigated in the same manner as above.

The ethylene used for this purpose was of  $98$  per cent. purity.

*Expt. 1.*—Temperature  $860^{\circ}$ .  $C_2H_4=32$ ;  $H_2=68$ .

Time (min.) .....	0	2	3	4	8	12	18	28	32	40
Pressure (mm.) ...	760	742	739	735	722	711	707	703	702	702

Final composition,  $C_2H_2$ , nil;  $C_2H_4=8.5$ ;  $CH_4=8.3$ ;  $CO=4.5$ .  
Contraction= $7.6$  per cent.

*Expt. 2.*—Temperature  $1000^{\circ}$ .  $C_2H_4=32$ ;  $H_2=68$ .

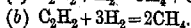
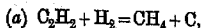
Time (mins.) .....	0	3	10	20	30	40	50	60	70	80	90	100	110
Pressure (mm.) .....	760	733	714	710	711	714	715	716	718	718	719	720	721

Final composition,  $C_2H_2$ , nil;  $C_2H_4=3.5$ ;  $CH_4=12.3$ ;  $CO=3.6$ .  
Contraction= $5.5$  per cent.

These results show that at temperatures between  $700^{\circ}$  and  $900^{\circ}$  acetylene reacts with hydrogen to give methane and ethylene. The amount of methane formed, as ascertained by analysis, was found

\* The composition of the gases is given in percentages.

to correspond approximately with the contraction, as would follow from either of the reactions below:



The amount of methane formed, however, was always considerably less than the loss of acetylene. This loss could not have arisen from the decomposition of the methane at first formed, as this reaction was found to be extremely slow, even when large quantities of methane were present. Consequently, even assuming all the methane to have been formed according to equation (a), some of the acetylene must have undergone decomposition according to the equation  $\text{C}_2\text{H}_2 = 2\text{C} + \text{H}_2$ , and a similar decomposition with the ethylene (compare Bone and Coward, *Trans.*, 1908, **93**, 1197).

It is also seen from these results that, in the form of apparatus used, in which about one-half of the total volume of gas was heated to the particular temperature, the decomposition of acetylene in presence of hydrogen into methane and into carbon and hydrogen takes place at  $720^\circ$  to the extent of one-half in about twenty minutes. At  $980^\circ$  seven-eighths is similarly decomposed in forty minutes. The reaction between ethylene and hydrogen also takes place at about the same rate. The decomposition of methane into carbon and hydrogen, on the other hand, was too slow to be measured.

It follows from these measurements that in the experiments made on the synthesis of hydrocarbons by the circulation method (p. 1802) at temperatures below  $1200$ – $1300^\circ$ , the acetylene or ethylene would be separated largely as such. Sufficient time had not been allowed for the formation of the quantities of methane obtained from the observed amounts of ethylene and acetylene. Consequently, most of the methane which was formed in these cases, and which was always largely in excess of the other hydrocarbons, must have arisen directly from the elements, or else through the intermediate formation of some hydrocarbon at present unknown.

At the higher temperatures of  $1500^\circ$  and upwards, the ethylene present would certainly account for most of the methane observed.

These results further show that the presence of ethylene will play a very large part in those experiments in which hydrogen was left in contact with the heated carbon over a long interval, even at  $1200^\circ$  (parts I and II). The amount of methane, on account of its comparatively great stability, would be raised above the equilibrium quantity at the temperature of the rod, on account of the polymerisation of the traces of ethylene formed with hydrogen in the cooler parts of the vessel.

The formation of methane from acetylene and hydrogen as con-

## 1810 SYNTHESIS OF HYDROCARBONS AT HIGH TEMPERATURES.

ducted with the heated porcelain tube is an interesting example of an intermediate product arising in quantities much larger than are permanently stable at the particular temperatures used.

The above work, which has demonstrated the synthesis of methane and also of ethylene at temperatures from  $1200^{\circ}$  upwards, still leaves undecided the question of the equilibrium between methane and hydrogen, and shows that this cannot be ascertained in the form of apparatus hitherto used.

Berthelot, using a method in which the whole of the reacting substances were at a uniform temperature, could detect no hydrocarbons at  $1200$ – $1300^{\circ}$ , but the porosity of the vessel probably led to their oxidation.

### *Summary of Results and Conclusions.*

The reaction between carbon and hydrogen has been investigated by quickly removing the products from the neighbourhood of the heated carbon, and circulating the gas in large quantities through charcoal cooled by liquid air. Any traces of hydrocarbons were thus retained in the charcoal by condensation, and afterwards analysed. At a temperature of  $1200^{\circ}$ , and at pressures from 10 to 60 cm., carbon was found to combine with hydrogen to give methane and ethylene, the rate of formation of the latter being about 1/100th that of the methane. The amount of acetylene formed at this temperature is very much less, and could not be detected.

Measurements which were made of the rate at which acetylene and ethylene react with hydrogen to give methane, show that the amount of the latter hydrocarbon formed in these circulation experiments could not all be attributed to the initial formation of ethylene. At higher temperatures the ratio of ethylene to methane increased, at  $1400^{\circ}$  the amounts found being in the proportion of 1 to 10. In this case the amount of methane formed from ethylene would, of course, be much greater than at  $1200^{\circ}$ .

At  $1650^{\circ}$  methane, ethylene, and acetylene are obtained, and, as at higher temperatures, the quantity of ethylene formed is about twice that of the acetylene.

Palladium in contact with the carbon was found to assist catalytically the formation of methane to the same degree as platinum, whilst silicon had no appreciable effect.

It was found that the presence of a highly charged electric field surrounding the carbon made no difference to the rate of formation of methane at temperatures between  $1200^{\circ}$  and  $1600^{\circ}$ , so that no complication is produced in the reaction by ionisation from heated

# CHAPMAN AND JONES: DECOMPOSITION OF DRY OZONE. 1811

en caused by carbon vapour distilling from the rod and reacting the cooler parts of the vessel, or minute particles of carbon are possibly dispersed from the rod and act similarly.

The formation of ethylene which has not before been observed, or suspected at these low temperatures, has, in this work, been detected at 1200°, and at 1400° it is comparable with the methane formed. The equilibria between the different hydrocarbons and hydrogen are now being investigated by the use of high gaseous pressures.

Part of the incidental expenses of this research have been borne by a grant from the Research Fund of the Chemical Society.

ELECTRO-CHEMICAL LABORATORY,  
THE UNIVERSITY, MANCHESTER.

## CCV.—*Decomposition of Dry Ozone.*

By DAVID LEONARD CHAPMAN and HERBERT EDWIN JONES.

REGULATION on the cause of the influence of moisture on chemical change may be said to have been started by H. B. Dixon's announcement of the striking fact that an otherwise explosive mixture of carbon monoxide and oxygen will not inflame after it has been thoroughly desiccated by long exposure to phosphoric oxide. The interest taken in this problem has, in the meantime, been maintained through the discovery (chiefly by Dixon and his pupils) of numerous other examples of water promoting chemical change. I. B. Baker, in particular, has submitted the question to a most exhaustive examination, and the information gathered by him has served to demonstrate the supremely important part played by moisture in chemical changes of the most varied types. Yet owing, no doubt, to the difficulty of obtaining quantitative information bearing on the subject, the phenomenon still remains, in the opinion of many, a mystery. No general hypothesis has, so far, gained universal acceptance. H. E. Armstrong, who holds firmly to Faraday's view that chemical change is essentially electrolytic in character, advances the explanation that water introduces into the system the possibility of electrolytic and reversed electrolytic processes taking place.\* J. J. Thomson postulates in the moist gas the

\* By electrolysis the author clearly contemplates a process differing in one essential particular from that which is commonly understood by the term. Electrolysis, in its accepted and perhaps restricted sense, can proceed only so long as a transference of electrons is rendered possible through the agency of a

presence of minute drops of water, in the vicinity of which (owing to the high specific inductive capacity of water) the electrostatic forces that bind the atoms together are diminished. Dixon favours, for the present, less general explanations, based on chemical facts.

In attempting to picture the mechanism of a chemical change on which water exerts an accelerative effect, it must be borne in mind that in some few cases of chemical change this agent appears to play an unimportant rôle.

As examples of such actions, the following may be cited:

(a) A dry mixture of cyanogen and oxygen inflames as easily as a mixture of the same composition containing moisture (H. B. Dixon, *Trans.*, 1886, **49**, 384).

(b) The dried halogens attack mercury with facility (W. A. Shenstone, *Trans.*, 1897, **71**, 471.)

(c) Thoroughly desiccated ozone is much less stable than the moist gas (W. A. Shenstone, *loc. cit.*)

It is manifest that a more exhaustive examination of such exceptional cases might, by shedding a fresh light on a relatively neglected aspect of the problem, indicate the right course to be taken in future attempts to discover a solution. The last of the cases quoted above has already received some attention at our hands, and in this research its investigation has been further pursued.

As stated above, Shenstone, in 1897, showed that dry ozone is so unstable that it cannot be prepared from pure oxygen, desiccated with phosphoric oxide, by the silent discharge in the ordinary way. Moreover, the stability of ozone was found by him to decrease as the amount of moisture in the oxygen from which it was produced was diminished. The conclusion was therefore drawn that moisture inhibits the reverting of ozone to oxygen. Armstrong maintained that the peculiar instability of dry ozone, observed by Shenstone, was not caused by the absence of moisture, but was due to the presence of oxides of nitrogen (formed by the continuous action of the discharge from adventitious nitrogen contained in the oxygen), which, as Andrews had shown, immediately destroy ozone. The probability of the truth of Armstrong's contention is supported by the following considerations.

If, as Shenstone asserts, water vapour inhibits the reverting of

conductor of the first class; whereas electrolysis in the sense in which it is employed by Armstrong denotes a process in which the transference of electrons takes place in a molecular grouping across ultramicroscopic distances without the intervention of a metallic conductor. The process conceived by Armstrong is manifestly more sensitive to changes of temperature than ordinary electrolysis.

due to oxygen, the fact is a unique example of a new type of catalysis—real negative catalysis. There is no established case of substance *per se* hindering the progress of a spontaneous chemical change. The so-called negative catalysts operate by modifying an agency which promotes the change.\*

Ozone, dried with concentrated sulphuric acid, does not become more stable on its being saturated with water vapour (see Chapman and Jones, *Trans.*, 1910, **97**, 2463, and other publications referred to in the paper).

A point in Armstrong's explanation of Shenstone's result needs further investigation. The explanation assumes that oxides of nitrogen are generated by the discharge with greater facility when the gas is dry. A few simple experiments will serve to demonstrate that this assumption is true, and to indicate the reason for the fact assumed.

*Experiment I.*†—Oxygen dried with sulphuric acid was passed through a Brodie ozone generator in action, and then through a long, horizontal tube, bent downwards about six inches from its end to permit of the exit being immersed in water. For about eight minutes the ozonised oxygen which had bubbled through the water was quite clear, but after that time it began to be filled with fine mist, which gradually increased in density. On warming the horizontal glass tube, a dense cloud was formed above the surface of the water. The ozone manifestly contained some hygroscopic substance, which condensed in a film on the surface of the glass and was volatilised on being warmed.

*Experiment II.*—A wash-bottle, containing concentrated sulphuric acid, was inserted between the ozone generator and the horizontal glass tube. This effectually prevented the formation of a cloud in the ozonised oxygen above the water.

*Experiment III.*—Dry air, mixed with a little nitrogen peroxide, was passed through water. No cloud was formed. The hygroscopic substance in question is not nitrogen peroxide.

*Experiment IV.*—Dry air, containing a little nitrogen peroxide, was allowed to mix with ozonised oxygen, and then passed through water. An extremely dense cloud was instantly formed. The

\* Inhibitors are apparently divisible into three classes:

(a) Photochemical inhibitors the action of which seems to be due to their property of modifying the energy which is the cause of chemical change (Burgess and Chapman, *Trans.*, 1906, **89**, 1399; Chapman and MacMahon, *Trans.*, 1909, **8**, 135, 959, 1717; 1910, **97**, 845; Chapman and Gee, this vol., p. 1726).

(b) Inhibitors the action of which depends on their combining with a positive catalyst.

(c) Inhibitors which "poison" a solid catalyst (Bredig and others).

† In performing these experiments one of us was assisted by Mr. Edwin Hopkinson.

hygroscopic substance is probably a compound produced by the action of ozone on the nitrogen peroxide, and is most likely nitric acid.

*Experiment V.*—The cloud produced when ozonised oxygen was passed through water was collected in moist glass wool. The water in the glass wool was found to contain nitric acid, but no nitrous acid.

It is obvious from the above experiments that in the presence of moisture the nitrogen peroxide is removed from ozonised oxygen as nitric acid, which condenses on the surface of the glass, and that the oxides of nitrogen are completely eliminated by the gas being brought into contact with concentrated sulphuric acid, so that the respective causes of ozone, prepared from moist oxygen, being more stable than that formed from the dry gas under similar conditions, and of ozone generated, according to the recommendation of Brodie, in the presence of concentrated sulphuric acid, being in a condition of maximum stability are no longer matters of doubt.

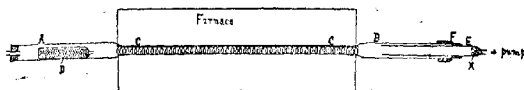
The ozonised oxygen employed by us in all our experiments has been collected in vessels containing concentrated sulphuric acid, and has been left in contact with the acid for several hours before use. We have already shown that the stability of ozone in a mixture of ozone and oxygen, treated in the above manner, is not increased nor appreciably decreased when the mixture is saturated with water vapour. Shenstone's statement that moist ozone is more stable than the partly desiccated gas is therefore incorrect; but it cannot, as yet, be affirmed that the presence of a very small quantity of water vapour is not essential to the progress of the change. The latter statement could, it is true, be made if it were known to be generally the case that the concentration of the water vapour and the rate of change were proportional in those changes for which water vapour is supposed to be necessary. From analogy, we should expect such a relation to hold. It is, however, possible, and has been occasionally assumed to be true (on grounds that are quite insufficient, however) that the rate of change rises very rapidly from zero to a limiting value as the concentration of the water vapour is increased, or, in other words, that the maximum effect can be obtained by the addition of a small amount of vapour. If such were the case, it might be found that, although two samples of ozone, of which one had been dried with concentrated sulphuric acid, and the other saturated with moisture, reverted to oxygen at the same rate, a specimen of the gas, dried by long exposure to phosphoric oxide, would prove to possess enhanced stability. Experiments conducted with the object of testing this possibility will be described later.

*The Preparation of Pure Phosphoric Oxide.*

The purification of phosphoric oxide by the distillation of the crude oxide in oxygen is both tedious and expensive. The yield is small, and the Jena-glass, after having been once used for the purpose, is completely destroyed. We find that the pure oxide can be prepared with little trouble and much less expense by the burning of phosphorus in air if certain precautions are taken to ensure complete oxidation. The apparatus we use for this purpose is depicted below (Fig. 1).

Two wide pieces of Jena-glass combustion tubing are fused, as shown in the figure, to a long, narrow piece of tube *C* of the same kind of glass. Into the tube *C* a spiral of platinum wire is inserted. The section of the combustion tube, marked *A*, encloses a hard glass tube *D*, which is closed at one end, and drawn out at the other to a narrow opening. This tube is filled with amorphous

FIG. 1.



phosphorus. A tube *E* of soft German glass is inserted into *B*, and held in position by a tightly fitting rubber band *F*. *E* contains a plug of glass wool *X*, in order to prevent the finely powdered oxide which collects in *E* from passing further along the tube. The tube *C* is heated to bright redness by means of the furnace, a rapid current of dry air being drawn through it with the aid of a pump connected to *E*. The temperature of the phosphorus in the vessel *D* is then very gradually raised until the vapour escapes and burns at the narrow aperture. By regulating the temperature, the size of the flame of burning phosphorus is kept quite small. If the combustion of the phosphorus is not too rapid, and the supply of air or oxygen is not deficient, the lower oxides of phosphorus are completely oxidised as they pass through the heated tube *C*, and the solid oxide which collects in the tube *E* answers to all the tests for purity given in Shenstone's paper. As Jena combustion glass is not attacked by the vapour of phosphoric oxide, the tube can be used many times for the same purpose. It is possible that the platinum spiral might be dispensed with.

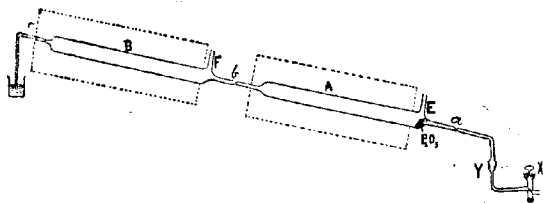


*Comparison of the Rate of Decomposition of thoroughly deoxygenated Ozone with that of Ozone dried with Concentrated Sulphuric Acid.*

The oxygen and ozonised oxygen were prepared and collected as described in our previous communication.

The tubes in which the ozonised oxygen was heated were constructed out of Jena combustion glass. Before being filled, they were thoroughly cleansed and dried, all the usual precautions being taken. Two tubes, *A* and *B*, as set up for the purpose of filling, are represented in Fig. 2. Each tube is provided with a side-tube *E* and *F*. Through one of these, say *E*, a plug of phosphoric oxide is introduced, and both the side-tubes are then closed in a similar manner by fusion with the oxy-hydrogen flame. Oxygen is then admitted to the apparatus through the tap *X*. The oxygen passes by way of the ground-glass connexion *Y* through the capillary tube

FIG. 2.



*a* into *A*, and thence through the capillary tube *b* into *B*; it escapes through the capillary tube *c*, the end of which dips under concentrated sulphuric acid. After all the air has been displaced by oxygen, the ozonised oxygen is permitted to enter, sufficient being passed through to ensure of the gas in *A* being of the same composition as that in *B*. The tubes *a*, *b*, and *c* are then closed before the oxy-hydrogen blowpipe at the constrictions shown in the figure. Both receptacles were then kept in the dark for periods of time varying in the separate experiments from ten days to six weeks.\* To decompose the ozone, the tubes are held in a vertical position with the side-tubes *E* and *F* below, and the top portions, indicated in the figure by dotted lines, surrounded with metal jackets (similar to those described in our previous papers), through both of which steam is passed for the same length of time. The time of heating varied from thirty minutes to one hour, these limits being selected because previous experience had shown that the proportion of ozone

\* Pure ozone decomposes extremely slowly at the ordinary temperature.

# CHAPMAN AND JONES; DECOMPOSITION OF DRY OZONE. 1817.

destroyed would, under the conditions of experiment, then lie between one-half and three-quarters of that originally present.

To analyse the contents of a tube, the gas was slowly driven out of the tube through a neutral solution of potassium iodide by a current of carbon dioxide, and after the solution of potassium iodide had been mixed with a little dilute sulphuric acid, the liberated iodine was titrated with a standard solution of sodium thiosulphate. The volume of each tube was measured after the experiment.

*Experiment I.*—The first pair of tubes, after they had been left in the dark for a fortnight, were completely immersed in a bath of boiling water for half an hour. On analysis of the contents, the tube in which the anhydride was enclosed was found to contain only half as much ozone as that in the other. That this result was due solely to the catalytic influence of the phosphoric oxide on the decomposition of the ozone is amply demonstrated by subsequent experiments.

*Experiment II.*—This experiment was performed in order to discover if the difference in the rates of decomposition in the two tubes due to the catalytic influence of the drying agent is sufficient to cause the percentage composition of the mixture in the one tube to be appreciably different from that in the other after the tubes had been left in the dark for three weeks. The contents of two tubes which had been left in the dark for the stated time were analysed, and the following results were obtained:

## *Tube A (containing drying agent).*

Ozone corresponding with iodine liberated	=	0.00564 gram.
Volume of the tube.....	=	63 c.c.
Ozone per litre.....	=	0.0895 gram.

## *Tube B.*

Ozone corresponding with iodine liberated...	=	0.00450 gram
Volume of tube .....	=	55 c.c.
Ozone per litre .....	=	0.0818 gram

The proportions of ozone in the two tubes are sufficiently close to show that the catalytic influence of the drying agent on the rate of decomposition of ozone at the ordinary temperature can be ignored. Experiment I, however, demonstrates the necessity of leaving the phosphoric oxide unheated. In the subsequent experiment therefore only the portions of the tubes above the side-tubes were heated in the steam-jackets. As the tubes were almost exactly similar, the proportion of hot to cool gas was approximately the same in both. The results are tabulated on p. 1818.

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Number of experiment.	Time of drying	Time of heating (minutes).	Ozone found. (gram).	Volume (c.c.).	Ozone per litre. (gram).
I. dry	3 weeks	30	0.0031	64	0.0484
not dry	—	—	0.0027	58	0.0466
II. dry	3 weeks	30	0.00268	55	0.0487
not dry	—	—	0.00274	56	0.0490
III. dry	10 days	45	0.00479	65	0.0737
not dry	—	—	0.00407	54	0.0754
IV. dry	2 weeks	60	0.00377	64	0.0588
not dry	—	—	0.00379	59	0.0642
V. dry	2 weeks	60	0.00443	57	0.0777
not dry	—	—	0.00435	55	0.0791

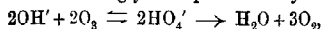
We deduce from former experiments that the amount of ozone destroyed during the heating would vary in the separate experiments from a little less than one-half to three-quarters of that initially present.

In our opinion, this investigation shows, with a degree of probability that almost amounts to certainty, that small quantities of water vapour do not exert an influence on the thermal decomposition of ozone. For if ozone ceases to decompose when it is absolutely deprived of moisture, it is almost incredible that there should not be a greater difference than is possible from the results of this and the previous research in the ratio of decomposition of the gas dried with phosphoric oxide, on the one hand, and saturated with water vapour, on the other.

The fact established in our last paper that, by increasing the partial pressure of the oxygen mixed with the ozone, no alteration in the rate of decomposition of the latter results, shows that the oxygen used in the experiments contained no catalyst for the change. That a catalyst was adhering to the inner surface of the glass and was volatilised when the tubes were heated to 100° is also improbable, firstly, because the tubes were strongly heated in a current of dry air before being filled, and secondly, because the presence of such a catalyst would have been indicated by discordant results. The experimental evidence favours the view that the decomposition of ozone can proceed by itself, without the intervention of any other substance.

The view expressed by Dixon years ago, and later supported by Shonstone, that some chemical changes can proceed without the aid of water, receives from this research substantial support. Furthermore, the work being quantitative in character, it enables us to take a step forward by expanding Dixon's conclusion with the statement that in one chemical change, at least, not only is the presence of water unnecessary, but it attended by an inappreciable effect.

To prevent misunderstanding, it may be well to point out that this research is no ground for the conclusion that water is not a weak catalyst for the decomposition of ozone. There are, on the contrary, strong reasons for thinking that it may be. Ozone, when it is passed into concentrated aqueous potassium or sodium hydroxides at a low temperature, furnishes yellowish-brown solutions, which are very unstable, rapidly evolving oxygen when the temperature is raised. The acidified yellow solutions do not contain hydrogen peroxide. In all probability therefore the solutions contain salts of a weak acid of the composition expressed by the formula  $H_2O_nO_3$ . It is by no means improbable that it is the ionised portion of the salt which is unstable, and that the changes in the solution can accordingly be represented by the equations:



it being assumed, for the sake of argument, that the ions contain but one molecule of ozone. If the above view of the decomposition of ozone by alkalis is correct, water and even steam must in some measure accelerate the reverting of ozone to oxygen. In the presence of moisture, most of the ozone is destroyed, however, without the assistance of the water, the number of hydroxyl ions being so small that their catalytic effect cannot be detected. It being assumed that the law of mass holds, the rate of decomposition of ozone would then be given by the equation:

$$\frac{d[O_3]}{dt} = A[O_3]^2 + B[O_3]^2[OH],$$

in which  $A$  and  $B$  are constants. In the above equation, the last term must be supposed to be negligible owing to the finite value of  $B$  and the infinitely small value of  $[OH]$ .

THE SIR LEOLINE JENKINS LABORATORIES,  
JESUS COLLEGE, OXFORD.

## CCVI.—*The Acid Character of Gallotannic Acid.*

By RAMNI PANIKER and EDMUND STIASNY.

IN spite of the large amount of experimental data which has accumulated on the subject of late, the chemical constitution of gallotannic acid is not settled beyond controversy. The problem naturally resolves itself into the following questions:

1. Is gallotannic acid a single substance or a mixture?
2. Is it a real acid, that is, one containing a free carboxyl group?

## 3. How is the optical activity to be accounted for?

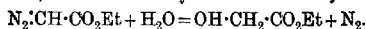
As to its homogeneity, different authors assume that it is a mixture of closely allied substances. Walden (*Ber.*, 1897, **30**, 3151) drew the above conclusion by studying its dialytic behaviour and the properties of the different products obtained by fractional precipitation. He also observed different optical activities for the various samples purified by different methods (compare Rosenheim and Schidrowitz, *Trans.*, 1898, **73**, 885; Dekker, *Ber.*, 1906, **39**, 2497; and Nierenstein, *Chem. Zeit.*, 1909, **33**, 126). Aweng (*Rev. Int. Falsif.*, 1898, **11**, 29) arrived at the same conclusion by studying its condensation products with formaldehyde. By means of capillary analytical experiments, Kunz-Krause (*Schweiz. Wochensch. Chem. Pharm.*, 1898, No. 38) found that a 5 per cent. aqueous solution of pure gallotannic acid gave two distinct capillary zones, leading him to the same conclusion as the previous authors. Finally, Nierenstein (*Ber.*, 1905, **38**, 3641; 1907, **40**, 917; 1908, **41**, 77, 3015; 1909, **42**, 1122, 3552; 1910, **43**, 628; *Chem. Zeit.*, 1907, **31**, 72; 1909, **33**, 15) explains the properties of gallotannic acid as due to a mixture of digallic acid and leucotannin.

As regards the acid character of gallotannic acid, expressed by the presence of a free carboxyl group in the well-known Schiff's formula,  $C_6H_2(OH)_3 \cdot CO \cdot O \cdot C_6H_2(OH)_2 \cdot CO_2H$ , several authors hold different views on the subject. Thus Böttinger (*Ber.*, 1884, **17**, 1503) found that benzoylgallotannic acid is insoluble in alkali. Dekker (*loc. cit.*) showed that the acetyl compound was insoluble in excess of *N*-sodium hydroxide even on boiling. Dekker therefore argued that no free carboxyl group could be present in the molecule, and cites the work of Walden (*Ber.*, 1898, **31**, 3170), who, from his electrical conductivity experiments, found such low figures for the affinity constant that he assumed gallotannic acid to be of a non-electrolytic nature, the small experimental figures being ascribed to impurities.

The present paper deals mainly with the acid character of gallotannic acid, but the question of its homogeneity is also considered.

## EXPERIMENTAL.

The determination of the hydron concentration of gallotannic acid was carried out by Fraenkel's method (*Zeitsch. physikal. Chem.*, 1907, **60**, 202), which is based on the evolution of nitrogen from diazoacetic ester, due to the catalytic influence of hydrions:



In investigations of a like nature (Spitalsky, *Zeitsch. anorg. Chem.*, 1907, **54**, 265; Holmberg, *Zeitsch. physikal. Chem.*, 1908,

62, 726), this method has given very satisfactory and concordant results.\*

The velocity of the reaction is calculated from the volume of nitrogen evolved at definite intervals of time:

$$\text{where } k = \frac{1}{0.4343t} \log \frac{a}{a-x},$$

$a$  = total value of nitrogen corresponding with a given concentration of the ester;

$x$  = volume of nitrogen evolved in time  $t$ .

The use of a glass flask was precluded by the appreciable neutralisation of hydrogen ions due to the alkalinity of the glass, especially in the case of weak organic acids. Quartz was found to be a satisfactory substitute for glass, and all recorded experiments were performed in a quartz flask.

#### *Purification of Gallotannic Acid.*

*Method I.*—Fifty grams of Kahlbaum's "extra pure tannic acid" were dissolved in 500 c.c. of water, and precipitated by means of a saturated solution of pure sodium chloride. The precipitate was repeatedly washed on the filter with the salt solution, again dissolved in a small quantity of water, and salted out. This salting-out process was repeated half-a-dozen times, and the product finally dried in a vacuum at a low temperature. The dried mass was then extracted with freshly distilled methyl acetate, the filtrate evaporated in a vacuum at the laboratory temperature, and dried until free from all traces of the solvent. The sample so obtained was by no means free from traces of gallic acid, which are invariably carried down with the precipitate during the salting-out operations.

*Method II.*—This method was that described by Rosenheim and Schidrowitz (Trans., 1898, **73**, 882), but depending as it does on the phenomenon of distribution of a substance between two solvents, it is by no means a perfect one.

The small amount of gallic acid which is always left behind in the purified sample introduces a greater variation in the degree of acidity than in the values obtained by the authors above referred to for the specific rotatory power of the substance.

*Method III.*—(1) This consisted in neutralisation by means of sodium hydrogen carbonate and extraction with ethyl acetate.†

The commercial product was first purified from all resinous and

\* For the preparation of the diazo-ester and a detailed description of the apparatus used, see Klages, *Ber.*, 1903, **36**, 1506; Fraenkel, *Zeitsch. physikal. Chem.*, 1902, **40**, 202; 1904, **47**, 185.

† This method was suggested to us by Mr. A. G. Perkin, to whom we are indebted for the great interest he took in this work.

colouring matter by repeatedly shaking the acetone solution with ether (as in method II), and the residue dried as before. The product so obtained was dissolved in a small quantity of water. To avoid the presence of any normal carbonate, a current of carbon dioxide was passed through a saturated solution of sodium hydrogen carbonate for about twenty minutes. The aqueous solution of the tannin was similarly freed from oxygen, and neutralised with the bicarbonate solution until it was faintly alkaline to litmus.

The solution was then extracted three times with freshly distilled ethyl acetate. The extract so obtained was washed with small quantities of water until free from traces of alkali, concentrated in a vacuum at the ordinary temperature, and precipitated by means of pure dry benzene. The white precipitate so obtained was boiled with benzene to remove traces of the ester, filtered, and finally dried in the vacuum oven for four hours. The acidity of the product was then tested.

(2) The above purification was then repeated, using more of the bicarbonate solution, so that the liquid was more strongly alkaline than in the previous case. The product so obtained was tested for acidity.

(3) Repeating the process of purification for a third time, the aqueous solution of the substance was finally precipitated with the bicarbonate solution, and extracted as before. The product was again examined as in the two previous cases.

(4) The filtrate obtained after precipitation with the bicarbonate solution was partly neutralised with hydrochloric acid, and extracted with ethyl acetate, washed, concentrated, and finally precipitated with benzene. In the place of a white, amorphous precipitate, as obtained in the last case, a dark, viscous mass was produced, which, when dried, was greyish-white. The acidity of this product was also noted.

Owing to the insolubility of sodium gallate and other allied salts in ethyl acetate, this method is an excellent means of purifying gallotannic acid. The products so obtained are invariably free from even traces of sodium.

#### *Catalysis of Ethyl Diazoacetate.*

Weak electrolytes, tested according to this method, yielded the following values for  $k$ :

TABLE I.

	<i>k</i> .
Gallic acid .....	0.01337
Protocatechuic acid .....	0.01122
$\beta$ -Resorcylic acid .....	0.04999
Salicylic acid .....	0.0751
Pyrogallol .....	0.000081
Boric acid .....	0.000065

A summary of the results obtained with gallotannic acid is given in table III.

The following table gives details of a typical experiment with gallotannic acid:

TABLE II.

Catalyst: Gallotannic acid (0.3244 gram); method II; fourth purification.

Concentration of ester, 0.2050 gram in 20.2 c.c. Mean pressure, 749.6 mm.  $a = 40.28$  c.c. ( $x' = x$  at N.T.P.)

(mins.).	Temp.	<i>x</i> c.c.	<i>x'</i> c.c.*	<i>a - x'</i> .	<i>k</i> .
30	14.0°	2.605	2.41	37.87	0.002052
40	13.5	3.60	3.33	36.95	0.002153
50	13.5	4.60	4.26	36.02	0.002236
60	13.5	5.60	5.09	35.19	0.002252
70	13.5	6.40	5.91	34.37	0.002267
80	13.5	7.30	6.74	33.54	0.002289
90	13.5	8.20	7.57	32.71	0.002318
100	13.5	9.10	8.40	31.83	0.002339
110	13.5	9.90	9.14	31.14	0.002340
120	13.5	10.605	9.79	30.49	0.002321
130	13.5	11.40	10.52	29.76	0.002328
140	13.5	12.20	11.26	29.02	0.002342
150	13.5	12.85	11.86	28.42	0.002325
160	13.5	13.60	12.56	27.72	0.002336
170	13.5	14.30	13.20	27.08	0.002336
180	13.5	15.00	13.84	26.44	0.002339
225	13.5	18.00	16.82	23.66	0.002365
250	13.5	19.50	18.00	22.28	0.002369
265	13.5	20.40	18.83	21.45	0.002377
280	13.0	21.20	19.66	20.82	0.002391
300	13.0	22.30	20.68	19.60	0.002396
330	13.0	23.65	21.93	18.35	0.002383
360	13.0	25.05	23.23	17.05	0.002388

Mean value of  $k = 231 \times 10^{-5}$ .  $C_H = 6 \times 10^{-5}$ .†

\* In calculating this quantity allowance must, of course, be made for the tension of aqueous vapour as  $x$  is measured moist.

† The value of  $C_H$  is calculated by using Fraenkel's factor for aqueous solutions:  $k/C_H = 38.5$ .



TABLE III.

The values of  $k$  are compared with the specific rotatory power of each sample.

Purification.		Conc., gram in 20.2 c.c.	$k$ .	$C_H$ .	$[\alpha]_D^{25}$ .	Remarks.
Method.	Order.					
"	I.	0.322	$328 \times 10^{-5}$	$8.5 \times 10^{-5}$	—	Rich in gallic acid
"	II. 1st	0.322	$422 \times 10^{-5}$	$11.5 \times 10^{-5}$	+73.29°	Rich in gallic acid
"	" 2nd	0.33832	$240 \times 10^{-5}$	$6.2 \times 10^{-5}$	+72.12	{ Contained traces of gallic acid Seems free from gallic acid Seems free from gallic acid
"	" 3rd	0.32888	$198 \times 10^{-5}$	$5.1 \times 10^{-5}$	+72.37	
"	" 4th	0.3244	$231 \times 10^{-5}$	$6.0 \times 10^{-5}$	+70.90	
"	III. 1st	0.33472	$224 \times 10^{-5}$	$5.8 \times 10^{-5}$	+56.76	{ Free from even traces of gallic acid Free from even traces of gallic acid Free from even traces of gallic acid
"	" 2nd	0.30128	$148 \times 10^{-5}$	$3.8 \times 10^{-5}$	+64.72	
"	" 3rd	0.31592	$112 \times 10^{-5}$	$2.9 \times 10^{-5}$	+69.60	
"	" ex- tracted from filtrate [III(4)]	0.32408	$214 \times 10^{-5}$	$5.6 \times 10^{-5}$	+65.10	{ Free from even traces of gallic acid

*A Comparative Review of the Different Methods of Purification of Gallotannic Acid.*

*Method I* (Precipitation by means of sodium chloride) is not sufficient to get rid of all gallic acid from the commercial sample. A sample which was salted out twenty-four times still gave, after extraction with ethyl acetate or alcohol, a faint gallic acid reaction with potassium cyanide. This fact is clearly shown by the high values obtained for  $k$  and  $C_H$ .

*Method II* (Unequal distribution of gallic and gallotannic acids in ether and acetone) is a tedious one, and it is never possible to obtain a sample completely free from gallic acid. It can be seen from the tables that as the purification proceeds, the velocity constant, and consequently the hydron concentration, both diminish and approximate to a constant value.

*Method III* (Insolubility of sodium gallate in acetic ether) is by far the best which has been employed for the complete separation of gallic acid impurity from gallotannin. Unlike method II, even

the first fraction is so thoroughly free from gallic acid that we might with sufficient justification state that the hydrogen concentration  $5.8 \times 10^{-6}$  (see table) is outside the influence of gallic acid.

*Conditions which Govern the Progress of the Reaction.*

The temperature-coefficient of the reaction, judging from analogy to similar catalytic reactions, is by no means negligible. A difference of 0.25 to 0.5 which the thermostat had shown during the course of some experiments is perhaps sufficient in the majority of cases to account for the deviation which in certain cases  $K$  exhibits from its mean value.

The rate of evolution of nitrogen as measured by the nitrometer readings is considerably influenced by the character of the solution as well. When it is of a colloidal character, as with gallotannic acid solutions, a considerable amount of the gas is retained on the surface of the solution in the reaction flask, which consequently escapes measurement, and leads to a variation in the observed rate of the reaction.

*Affinity Constant and Optical Activity.*

No proportionality seems to exist between the specific rotatory power of the substance and its velocity constant. This relationship seems to depend largely on the method of purification employed, and is also governed by the amount of gallic acid impurity left in the sample.

Purification by method II, based on the work of Rosenheim and Schidrowitz, gives a substance with constant values for  $k$  and  $[\alpha]_D$ , and judged alone it would seem to indicate that gallotannic acid is an acid of constant rotatory power and of definite acidity. When we proceed to purify the same substance according to method III, a perceptible increase in the value of  $[\alpha]_D$  manifests itself as the value of  $k$  diminishes with the order of purification. This would naturally indicate a partial differentiation of the proximate constituents.

This method has already been stated to yield a product free from gallic acid. As is shown by the figures given in the table, the value of  $[\alpha]_D$  in this case is not so high as that of any of the purified samples under method II. Further, the acidity of the products in this case approximate to a minimum value. Moreover, by extracting the neutralised product from the mother liquor according to method III(4), a substance is produced which gives a velocity constant with almost double the value obtained in the case of the third sample (method III).

If these are two different chemical individuals, then naturally the one must be twice as strong as the other in its chemical affinity. These facts do not allow of the conclusion that we are here dealing with a homogeneous substance.

To compare the degree of dissociation of gallotannic acid with that of any other weak organic acid like gallic, we should naturally have some idea of the molecular weight of the substance in aqueous solution. According to Sabanéeff, gallotannic acid has a molecular weight of 1322 in water, but it is evident that this number has no molecular significance, inasmuch as the ordinary osmotic methods cannot be used for the determination of molecular weight of substances in a colloidal solution.

The fact that gallotannic acid can be divided into two parts by saturating the solution with sodium hydrogen carbonate, the one part being soluble in ethyl acetate, whilst the other forms a sodium salt which, on acidification, is capable of being extracted with ethyl acetate, points to the fact that we have here to deal with a mixture of two or more substances of different degrees of acidity.

This view is favoured by the fact that the substance extracted direct after neutralisation with sodium hydrogen carbonate is only half as acid as that which is set free on acidifying the sodium salt in solution. The difference in the values of  $k$  and  $[\alpha]_D$  shown by different samples purified after different methods also support this view.

Another observation may also be mentioned, although it still wants further investigation. If the white, amorphous precipitate obtained by salting out the solution of gallotannic acid is dissolved in absolute alcohol and treated with an absolute alcoholic solution of potassium acetate, a precipitate is formed, which in similar case has been shown by A. G. Perkin (Trans., 1908, 83, 129) to be the potassium salt of the acid or an oxonium salt. This precipitate was washed with absolute alcohol and treated with pure ethyl acetate to remove traces of any free gallotannic acid. It was then filtered, dried, and analysed. The following analytical figures were obtained, which, when calculated, seems to agree with the unimolecular formula  $C_{14}H_9O_9K$  for the potassium salt:

0.4383 gave 0.1032  $K_2SO_4$ .  $K=10.6$ .

$C_{14}H_9O_9K$  requires  $K=10.8$  per cent.

The optical inactivity of this potassium salt and the optical behaviour of gallotannic acid, prepared from the former, will form the subject of a special paper, which, we hope, will throw some light on the constitution of gallotannic acid.

*Summary.*

The foregoing experiments seem to be in favour of the view that allotannic acid is a mixture of two or more chemical individuals, possibly of an allied character (compare Kunz-Krause, Walden, and Tweng, Nierenstein). On the other hand, our observations do not agree with the view of Böttiger, Walden, and Dekker that galloannic acid has no free carboxyl group, as the affinity constant found by us is distinctly of a higher order than those of phenols.

UNIVERSITY, LEEDS.

CCVII.—*Bimolecular Glycollaldehyde.*

By NIAL PATRICK McCLELAND.

It has often been the custom to make a distinction between "association" and "polymerisation." The former has been regarded as a physical phenomenon consisting in the aggregation of whole molecules, whereas the latter is generally classed as a chemical process, and the constitution of the polymerised forms is expressed in terms of atomic linking.

At present the prevailing view appears to be that the two phenomena are of the same kind, differing only in degree, and it has been found necessary to evolve hypotheses of "latent," "auxiliary," and "contra" valencies to explain the constitutions of the resulting substances. Practically the question may be merely one of stability, that is to say, the difference between "association" and "polymerisation" as ordinarily defined may lie only in the fact that polymerised forms can be definitely isolated as such between wide limits of temperature, pressure, and so on, whereas the degree of association depends entirely on the conditions.

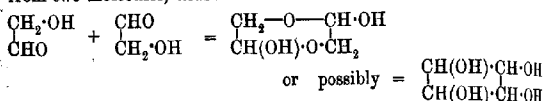
Now Fenton and Jackson observed (*Trans.*, 1899, 75, 575) that the molecular weight of crystalline glycollaldehyde in a freshly prepared aqueous solution is 120, that is to say, double the value expected from the formula  $\text{HO}\cdot\text{CH}_2\cdot\text{CHO}$ , and, further, that it actually falls to the normal value on keeping.

Similar behaviour has been observed in the related substances acetaldehyde and dihydroxyacetone by Wohl (*Ber.*, 1898, 31, 94) and Bertrand (*Compt. rend.*, 1899, 129, 341) respectively.

At Dr. Fenton's suggestion the author has investigated this change of state in the case of glycollaldehyde with the object of ascertaining its general character as an association or polymerisation phenomenon in the sense indicated above.

Bertrand concluded that the change observed by him was due to molecular dissociation. He seems to have based his conclusion partly on an observation that the molecular weight of the liquid formed by the melting of crystalline dihydroxyacetone was almost normal in solution, suggesting that the liquid was the unassociated form, and partly on the fact that, although the crystalline substance is sparingly soluble in alcohol and ether, yet on warming it readily dissolves, and does not recrystallise on cooling; reasons are given below for concluding that the former observation is erroneous; the latter can obviously be easily explained otherwise.

Wohl suggested that the crystalline form is a sort of acetal formed from two molecules, thus:



in which case the change in aqueous solution would be due to hydrolysis, with the formation of an ortho-aldehyde.

The investigation was carried out in the following way:

First, the dissociation of glycollaldehyde in aqueous solution was investigated with a view to ascertaining the influence of dilution on the rate.

Next, the molecular state in other solvents was studied. The solvents tried were methyl and ethyl alcohols, acetone, acetonitrile, pyridine, formic and acetic acids.

It was expected that if the change was due to hydrolysis, alcohols would bring it about almost as readily as water, possibly with the formation of acetals of the normal type, the other solvents not at all; whilst on the supposition that the bimolecular state is an example of association, solvents would probably be effective in the order of their dissociating powers.

The vapour density was also determined somewhat above the boiling point, and Mr. Purvis kindly photographed the absorption spectra of the two forms in solution.

The glycollaldehyde was prepared by the method described by Fenton (*Trans.*, 1905, 87, 817). A pyridine solution is formed from dihydroxymaleic acid, and is distilled in a vacuum; finally, glycollaldehyde crystallises out on nucleating the syrup obtained by evaporating the pyridine in a desiccator. During the latter part of the distillation (when all the pyridine has passed over), crystals are frequently formed in the tube, showing that they can form spontaneously.

Crystals have also been obtained from an aqueous solution, but any trace of impurity seems to prevent their formation.

The glycollaldehyde so obtained melts at 96—97°, forming a syrupy liquid, which, when cooled, does not crystallise for several days. This liquid appears to be identical with the syrup mentioned above. The yield is very poor, about 0.5 to 1 per cent. of the calculated (starting from tartaric acid). Owing to the cost, it was essential to work on a very small scale throughout.

*Dissociation Rate in Water.*

This was studied by making successive determinations of the apparent molecular weight in aqueous solution, using the cryoscopic method. Between readings, the solution was kept surrounded by ice.

The continual change of temperature necessary for each reading caused the experimental error to be somewhat great.

$t$  = time of observation in minutes after the first reading.

$m$  = calculated molecular weight.

$C$  = concentration of double molecules, taking the initial value as the unit,

so that  $C = \frac{M - 60}{60}$ ,

$k = \frac{1}{t' - t} \log_e \frac{C}{C'}$ , where  $C'$  and  $t'$  refer to the last reading given.

In this way it was hoped that the error due to the fact that it took an appreciable time to dissolve the whole of the substance would be minimised.

The molecular depression for water was taken to be 18.7.

(1) 0.4212 gram of substance in 20.80 of water (1 in 49.4).

$t$ .	$\Delta$ .	$m$ .	$C$ .	$k$ .
—	0.387	114.1	0.402	0.0023
30	0.401	110.1	0.835	0.0020
60	0.417	106.1	0.768	0.0020
95	0.429	103.0	0.717	0.0020
130	0.438	101.0	0.683	0.0021
160	0.449	98.5	0.642	0.0021
220	0.471	93.9	0.565	0.0022
270	0.489	90.4	0.507	—

Mean,  $k = 0.00210$ .

(2) 0.1831 gram in 16.56 (1 in 90.4).

$t$ .	$\Delta$ .	$m$ .	$C$ .	$k$ .
—	0.182	113.6	0.373	0.0030
60	0.198	104.4	0.740	0.0030
130	0.219	94.4	0.573	0.0028
190	0.231	87.4	0.457	0.0023
315	0.256	80.8	0.347	0.0033
330	0.259	79.8	0.330	—

Mean (excluding 4th value),  $k = 0.00303$ .

(3) 0.1128 gram in 31.91 (1 in 283).

It was found that  $k=0.00561$ .

The above results show that the reaction is, as might be expected, unimolecular, that is,  $C_4H_8O_4 \rightarrow 2C_2H_4O_2$ , and that the rate increases with the dilution.

The effect of temperature has not been studied quantitatively, but it has been observed that at  $20^\circ$  the change takes place with extreme rapidity.

So far as can be observed, the dissociation in dilute solutions is complete, but since crystals can be obtained from an aqueous solution it follows that association must take place in strong solutions.

#### *The Liquid Form in Water.*

The molecular weight in water was determined.

Solvent (grams).	Substance (gram).	$\Delta t$ .	M.W.	
1. 25.02	0.1946	0.118	123.0	fresh solution
		0.139	100.8	} on keeping
		0.149	97.4	
2. 15.43	0.1049	0.119	106.9	fresh solution
		0.194	65.5	on keeping

Whence it appears that the liquid form exhibits the same behaviour as the solid form.

Bertrand states, as mentioned above, that the molecular weight of a solution in water of liquid dihydroxyacetone is almost normal (105, normal value=90). He mentions, however, that it took twenty-five minutes to cool the solution to freezing point. If, as appears possible, he started with the solution at the ordinary temperature, it is natural that dissociation would take place very rapidly at first.

#### *Molecular State in Solvents other than Water.*

The solvents are taken in the order of their dissociating powers. All were purified carefully before using.

#### *Formic Acid.*

The cryoscopic method was used for this solvent. Const. =  $27.7$ .

Solvent (grams).	Substance (gram).	$\Delta t$ .	M.W.
22.13	0.1517	0.279	67.5
		0.439	42.9

That the molecular weight falls below 60 may be explained by assuming that esterification takes place in addition to dissociation.

one molecule of bimolecular glycollaldehyde giving rise to 4 molecules, 2 of unimolecular formate and 2 of water.

The same results were obtained when acetic acid was used as solvent; it was noticed that the apparent molecular weight gradually sank to 30.

It is concluded that in formic and acetic acids dissociation readily takes place, apparently accompanied by esterification.

#### *Methyl Alcohol.*

The molecular weight was observed by the boiling-point method, using Beckmann's apparatus.

The molecular elevation is 8.80.

Solvent (grams).	Substance (gram).	E.	M.W.
1. 40.61	0.2163	0.058 0.074	81.0 after 30 minutes' boiling 68.5 " 50 " "
2. 40.02	0.2828	0.059 0.079 0.091	105.6 " 15 " " 79.0 " 30 " " 68.5 " 45 " "

It appears, then, that dissociation takes place in methyl alcohol on boiling, although far less rapidly than in water and formic acid.

The experimental error was too great to permit the rate to be determined satisfactorily.

#### *Acetonitrile.*

The pure solvent boiled at 80.0°. The molecular elevation is 14.39.

Solvent (grams).	Substance (gram).	E.	M.W.
1. 40.92	0.2898	0.090 0.134	113.0 after 20 minutes' boiling 76.0 " 45 " "
2. 20.38	0.3330	0.156 0.178 0.201 0.236	108.2 " 20 " " 95.0 " 40 " " 84.0 " 60 " " 71.6 " 90 " "

Therefore, dissociation takes place in acetonitrile somewhat less rapidly than in methyl alcohol.

#### *Ethyl Alcohol.*

The molecular weight in a fresh solution was found by using Walker's method:

0.3871 gram in 15.8 c.c. gave E 0.31°. M.W.=123.1.

0.1560 " 19.5 c.c. " E 0.11°. M.W.=113.5.

A solution was then boiled under reflux for five hours. After this time the molecular weight was determined, and it was found that almost complete dissociation had taken place:



1832 McCLELAND: BIMOLECULAR GLYCOLLALDEHYDE.

0.4004 gram in 32.39 grams gave E 0.180°. M.W. = 79.0.

0.4004 „ 32.39 „ „ E 0.192°. M.W. = 74.1 thirty-five minutes later.

*Acetone.*

A solution was boiled for five hours, as before.

Substance (grams).	Solvent (gram).	E.	M.W.
32.39	0.4004	0.192	106.0
		0.197	103.6
37.96	0.2660	0.136	85.0

A solution kept at the ordinary temperature for three weeks showed no trace of dissociation.

*Pyridine.*

The molecular state in pyridine was determined by Blackman's method (Trans., 1904, 85, 1474) under diminished pressure, using carbamide (M.W. = 60) as comparative substance. The results appeared to indicate that the substance was dissociated.

*Vapour Density.*

Hofmann's method was employed.

Since glycollaldehyde on heating tends to polymerise into a brown gum, it was necessary to heat rapidly; even so, however, traces of "browning" appeared.

This rapid heating prevented the mercury from being properly heated throughout. These two errors tend to cancel one another, and no allowance has been made for them.

The heating liquid used was aniline, which boils at 182°.

This temperature is well above the boiling point of glycollaldehyde, which observations in a vacuum place in the neighbourhood of 150°:

(1) 0.0218 gram gave 48.6 c.c. of vapour at 182°.

Barometer's height, 782 mm.

Height of mercury column, 602 mm. Correction for expansion, 19 mm.

Vapour pressure of mercury at 182° = 12 mm.

So pressure of the vapour = 187 mm.

Hence vapour density = 33.8.

(2) 0.0141 gram gave 43.7 c.c. of vapour at 182°.

Barometer height, 758 mm.

Height of mercury column, 622 mm. Correction, 20 mm.

So pressure of the vapour = 144 mm.

Hence vapour density = 31.5.

The vapour is therefore unassociated about 30 degrees above the boiling point.

The above results, namely, dissociation in solvents usually classed as dissociating, some of which have no hydrolysing power, coupled with dissociation in the vapour state, and with return to the bimolecular state on condensation, appear to point to the conclusion that in the bimolecular state we are dealing with the phenomenon of association, that is, linking of two whole molecules, rather than chemical interaction between them. The abnormal feature of this case lies in the fact that dissociation is by no means immediate. It is possible, however, that in other cases, where a substance has been found partly associated in a solvent, true equilibrium may not have been reached.

An observation has been made, showing a chemical difference between the two forms.

#### *Action of Phenylhydrazine.*

When phenylhydrazine is added to an aqueous solution, a yellow osazone (m. p. 169—170°) separates; if, however, phenylhydrazine is added to a fresh alcoholic solution, no action whatever takes place, and on evaporating the alcohol the aldehyde appears to have dissolved in the phenylhydrazine.

This suggests that the CO group is absent from the associated form.

#### *Absorption Spectrum.*

A N/100-solution in alcohol of the solid glycollaldehyde was made, and its absorption spectrum observed in the usual way, through varying thicknesses.

Four well-marked bands were observed, and through a thickness of 15 mm. the centres of maximum absorption of the bands were  $\lambda$  2615,  $\lambda$  2550,  $\lambda$  2495,  $\lambda$  2445, and through a thickness of 42 mm. general absorption began at  $\lambda$  2645.

A N/100-solution in water was also examined; no bands were observed. The positions at which general absorption began through 15 mm. and 45 mm. were  $\lambda$  2270 and  $\lambda$  2290 respectively.

These results prove that the conditions of the dissolved substances were entirely different in the two cases (for it is extremely unlikely that the bands are due to the solvent itself).

#### *Specific Gravity and Refractive Power of the Liquid Form.*

At 100, 0.2035 c.c. weighed 0.2729 gram.  $D = 1.372$ .

0.3158 c.c. " 0.4300 "  $D = 1.361$ .

Mean.....1.366.

At 16° the density was obtained by measuring the length which a known weight of the liquid form occupied in a calibrated tube.

It was found that 0.6122 gram of mercury occupied 5.72 cm. of the tube,

and (1) 0.1540 gram substance occupied 14.12 cm.  $D = 1.385$ .

(2) 0.1277 " " " 11.60 cm.  $D = 1.397$ .

Mean.....1.391.

From the above, by extrapolation, the density at 11° = 1.393.

At 11° it was observed that  $\mu_w = 1.4811$  (Lorentz formula).

Hence  $M_D = 24.51$ .

Twice the calculated value for  $\text{HO} \cdot \text{CH}_2 \cdot \text{CHO}$  is 26.39.

From the above results the author concludes that the abnormal molecular weight of glycollaldehyde in the pure form is due to a phenomenon which is on the border line between "association" and "polymerisation," that is, association where the associated form is not extremely unstable.

It is suggested that the constitution in the bimolecular state is represented by the formula  $\text{HO} \cdot \text{CH}_2 \cdot \text{CH} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{CH} \cdot \text{CH}_2 \cdot \text{OH}$ , the

calculated value for the refractive power for which is 24.82 (not making any allowance for the ring formation), agreeing fairly well with the observed value. Similar formulæ suggest themselves in the cases of crystalline dihydroxyacetone and glyceraldehyde. Support is given to this hypothesis by the fact that some ketones (where no acetal formation is possible) and amides are associated. Aldehydes also appear to be capable of bimolecular association, for it has been observed that when gaseous formaldehyde is passed into chloroform (an extremely non-dissociating solvent) a substance having the formula  $\text{C}_2\text{H}_4\text{O}_2$  is obtained (*Pharm. Zeit.*, 1904, **49**, 608). In these cases the cohesion between the two molecules is far less intense than in the case considered above, in which it perhaps is due to some influence exerted by the hydroxyl group.

If the above constitution is assumed, the behaviour of the substance can be completely accounted for.

In the first place, it appears that solutions which give rise to absorption bands in the ultra-violet are generally those of substances which contain unsaturated rings admitting of alternations of linking, the bands being perhaps due to vibrations from one form of linking to another. In the case of glycollaldehyde, this can occur through

the alternation of the forms  $\text{C} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C}$  and  $\text{C}:\text{O}:\text{O}:\text{C}$ . Secondly, it

appears probable that a system of the above type is not very firmly linked up, and therefore will be liable to rupture if intense vibrations are set up.

It is suggested that solvents have the power either to intensify or damp the vibrations of the molecules of solutes, on account of the vibrations of their own molecules. Where the vibrations are intensified the solvent is a dissociating one, and it is particularly noticeable that those solvents are most strongly dissociating the molecules of which are most strongly associated, and so are in a state of vibration of a character similar to those of the solute.

In conclusion, the author desires to record his great indebtedness to Dr. Fenton for his very kind advice throughout the work, and to Mr. Purvis for photographing the absorption spectra and suggesting their interpretation.

UNIVERSITY CHEMICAL LABORATORY,  
CAMBRIDGE.

#### CCVIII.—*The Aerial Oxidation (Rusting) of Metals.*

By WYNDHAM ROWLAND DUNSTAN and JOHN RICHARD HILL.

SINCE the last communication (Trans., 1905, **87**, 1548; also Proc., 1907, **23**, 63) was made to the Chemical Society on this subject by one of the present authors in continuation of previous work, from which it was concluded that the presence of carbonic acid or of any acid is not essential to the rusting of iron, for which only dissolved oxygen and iron are the necessary conditions, several other investigators have made contributions in this field, the most important of these being that of Tilden (Trans., 1908, **93**, 1356), who has confirmed this conclusion. For the most part the other contributions have been made with the object of supporting the former view that carbonic acid is an essential feature in this process. The results presented by one of the present authors and his collaborators, by Whitney, and by Tilden, are, however, conclusive in showing that the older view must be abandoned. There is, moreover, no reason to believe that the mechanism of the reaction in the case of the rusting of iron differs essentially from that of other metals. There are a few points in which it has been supposed to differ, but it will now be shown that these are unimportant, and in no sense radical differences. What has now to be sought is a satisfactory explanation of the fact of the aerial oxidation, not only of iron, but of all those metals which possess this property.

In the previous paper it was held as a working hypothesis that the rusting of iron involves the intermediate formation of hydrogen peroxide, as in the case of the other metals. Support for this view

was obtained from the action of the various reagents which inhibit rusting and also destroy hydrogen peroxide, and as a working hypothesis it has done good service.

The electrolytic (dissociation) theory advocated by Whitney, Walker, and others has been discussed in the previous paper, and shown not to be supported by fact. It is based on the assumption that iron passes into solution in pure water by replacement of the hydrogen ions before rusting takes place. Tilden also apparently adopts this theory, but combines with it the view that impurities in the iron play an important rôle by setting up local electrolytic action. According to the electrolytic (dissociation) theory, however, pure iron should dissolve in pure water. The question of impurities, and the electrolytic action produced by these, is quite a distinct problem. The more recent fact established by Lambert and Thomson (*Trans.*, 1910, **97**, 2426) that pure iron does not rust in pure water containing dissolved oxygen, is opposed to the electrolytic (dissociation) theory of rusting, and is in accordance with the general experience that chemical change is invariably greatly retarded when highly purified materials are employed. Tilden also noticed a marked difference in behaviour between iron which has previously been treated with chromic acid and that which has not, an important point which is dealt with in the present paper.

The observation of these authors that slightly impure iron rusts without the presence of carbonic acid, or of any other acid, supports the conclusion arrived at by one of us in previous communications.

All these hypotheses and theories claim with varying degrees of success to explain the action of the various reagents which inhibit rusting. The carbonic acid and electrolytic theories are inferred from the circumstance that all alkalis inhibit rusting, but both theories are disproved by direct experimental evidence which cannot be disregarded. Beyond this, however, these theories make no serious attempt to explain the inhibiting action of other agents, such as chromic acid and its potassium salts, potassium iodate, permanganate, and ferrocyanide, and hydrogen peroxide. The action of chromic acid is no doubt to be ascribed to its rendering the iron passive, but no explanation has been advanced so far to explain the action of other inhibiting agents.

On the other hand, the suggestion that hydrogen peroxide is concerned has been much more successful as a working hypothesis in affording, at any rate, some reason for the action of the inhibiting agents, and in suggesting new lines of work. But here also the explanation is not wholly satisfactory or complete, since it now appears that there are some substances which decompose hydrogen peroxide, but do not inhibit rusting.

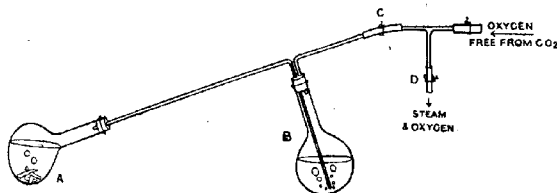
The action of the inhibiting agents is therefore a stumbling-block to any complete explanation of rusting. It is one of the main objects of this paper to throw further light on this question, and it will be shown that all inhibiting agents owe their action to the same cause, which differs from that ascribed to them by any of the explanations so far suggested.

### EXPERIMENTAL.

#### *The Solubility of Iron in Water.*

Before proceeding to a consideration of this subject, it is necessary to record the results of further experiments designed to test the applicability of the electrolytic theory, a subject which has been discussed in a previous paper. In addition to the results then presented, the following experiment was devised in order to deter-

Fig. 1.



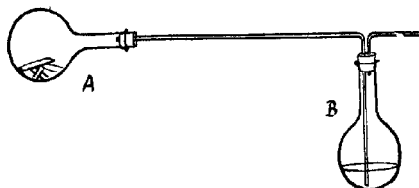
mine whether experimental evidence could be found for the assumed production of ferrous ions.

A and B were round Jena-glass flasks fitted with rubber stoppers and delivery tubes as shown. One of the delivery tubes from B was connected to a T-piece, one limb of which was open to the air and the other connected to an apparatus for supplying oxygen free from carbon dioxide. The flasks were three parts filled with distilled water, which was then boiled vigorously for some time. The steam from A escaped through B to the outlet in the T-piece. After boiling for a considerable time, the stopper of A was removed, and some bright strips of very pure iron\* were quickly dropped into the boiling water. The stopper was then replaced as quickly as possible. The boiling was continued for a quarter of an hour longer, and during the whole time a current of oxygen free from carbon dioxide was being passed through the outlet of the T-piece

\* The iron used in the experiments described in this and in the paper on the "Passivity of Iron and certain other Metals" was highly purified sheet iron. Sheet iron prepared by electrolysis behaved in a similar manner.

along with the steam. At the end of a quarter of an hour the flask *A* was allowed to cool, and became completely filled with boiling water from *B*. The water in *B* was boiled for a short time longer, and then the clip *C* was tightly screwed up. When the water in *A* and *B* had become quite cold, *D* was screwed up, thus stopping the exit of the oxygen. The clip *C* was then again unscrewed carefully, and a slow current of oxygen free from carbon dioxide drawn into *B*. When *B* was full of oxygen, the delivery tube, which had been drawn out at one point, was sealed. The stoppers were flooded with paraffin wax, and the apparatus fixed up in such a position that the delivery tube between *A* and *B* was horizontal, thus:

FIG. 2.



The apparatus was set aside, and examined from time to time for any signs of rust.

If the iron in *A* passes into solution in the water, as is assumed by the electrolytic theory, the ferrous ions so produced will diffuse from the flask *A* along the delivery tube towards *B*. Dissolved oxygen will at the same time be diffusing from *B* towards *A*; thus if the tube between *A* and *B* be sufficiently long, the ferrous ions should meet the dissolved oxygen, and produce rust somewhere in the tube. The length of the tube was 14 inches, and it was of narrow bore. Since no rust was visible in the flask *A* or in the tube after several months, it can be assumed that the oxygen was not diffusing towards *A* too rapidly. After six months the iron in *A* began to tarnish, and slowly developed a green film over the entire surface. After eight months the iron was completely and uniformly covered with an adherent green film, due to the formation of ferrous hydroxide along with a little ferric hydroxide, a mixture well known to produce a green colour. There was no sign of rust anywhere else in the flask or in the tube. From this it may safely be concluded that iron cannot rust until the oxygen actually reaches its surface, and that rusting in the absence of any acid is not preceded by solution of iron in the water.

*Objections to the Electrolytic Theory.*

The result of the above experiment confirms those previously recorded, and is in direct opposition to any theory which requires that the iron should pass into solution before forming rust. There are, however, many other objections to the electrolytic theory which it is convenient to enumerate here.

I. If iron passes into solution in pure water, the ferrous ions and the hydroxyl ions should form ferrous hydroxide, and hydrogen should be liberated. The process should be continuous, and appreciable amounts of these products should be formed. This, however, is not the case, as iron may be immersed in pure water for months without any change taking place. The upholders of the theory explain this fact away by assuming that the iron becomes polarised by the hydrogen which is liberated, thus stopping the action in its early stages; that on access of oxygen the latter acts as a depolariser, removing the film of hydrogen, and then only the process becomes continuous. There are four definite objections to this explanation:

(a) It is improbable that the iron could become permanently polarised until the water and the vacuous space above it had become saturated with hydrogen, in which case there would be a sufficient quantity both of hydrogen and ferrous hydroxide to be readily detected. Also iron can remain in boiling water for considerable periods without any apparent action taking place; and it is extremely improbable that under these conditions a complete film of hydrogen could be maintained un replenished.

(b) There is no evidence to show that dissolved oxygen can oxidise free hydrogen directly. The iron cannot facilitate this, since it is assumed to be kept out of contact with the water by the hydrogen film.

(c) If dissolved oxygen is able to depolarise the iron, other depolarising agents, such as potassium dichromate, chlorate, and nitrate, should effect the same result. This, however, is not the case.

(d) If iron can be polarised by the small concentration of hydrogen ions present in pure water, it should be at least equally polarised by a weak solution of carbon dioxide, since it is to be expected that the effect will be increased by raising the concentration of the hydrogen ions. This, however, is not the case. Many objections therefore arise to the supposition that iron becomes polarised in pure water.

II. Very dilute alkaline solutions allow copious rusting to occur, although their solutions are effective in fixing carbon dioxide. For



example, in presence of a solution of baryta (0.007 per cent.) iron will rust as copiously as it does in pure water with access of air freed from carbon dioxide. The concentration of hydroxyl ions in this solution is  $6.5 \times 10^{-4}$ . Assuming the concentration of the hydrogen ions and of the hydroxyl ions in pure water to be  $1.0 \times 10^{-7}$ , the product of the two is  $1.0 \times 10^{-14}$ . This product must remain constant, so that when the concentration of the hydroxyl ions is increased from  $10^{-7}$  to  $6.5 \times 10^{-4}$ , which is the case in the 0.007 per cent. baryta solution, the concentration of the hydrogen ions will fall from  $10^{-7}$  to  $1.538 \times 10^{-11}$ . Thus the concentration of the hydrogen ions in the 0.007 per cent. baryta solution is  $1/6500$ th of the concentration in pure water. According to the electrolytic theory, this enormous lowering of the concentration of the hydrogen ions should reduce any possible rusting to a negligible quantity. This is not the case, for, on the contrary, copious rusting occurs, and similar results are obtained with dilute solutions of other alkalis.

III. As will be shown later, the aerial oxidation of copper resembles that of iron. The electrolytic theory might therefore be expected to apply to the case of copper, and, indeed, of all metals. The electrolytic solution pressure of copper is  $10^{-12}$  atmosphere, a value much smaller than that of hydrogen, which is  $10^{-4}$  atmosphere. Consequently, no copper ions could replace the hydrogen ions in pure water, and thus pass into solution. According to the electrolytic theory, therefore, no oxidation should take place when copper is immersed in distilled water exposed to the air. This, however, is not the case, for copper does slowly oxidise in these circumstances.

IV. The electrolytic theory does not explain the action of the various inhibiting agents other than the alkalis; such as, for example, potassium chromate, and dichromate, iodate, ferrocyanide, and hydrogen peroxide. All these agents inhibit rusting, but according to the electrolytic theory most of these substances should assist it by depolarising the iron.

These are some of the difficulties which prevent the acceptance of the electrolytic theory as an adequate explanation of the rusting of iron, even if the fundamental fact of the solution of iron in pure water were proved to be correct.

Tilden describes an experiment in which water is repeatedly distilled from solid baryta on to iron contained in a silica boat in a vacuum. This experiment has been repeated by us with the same result, namely, the iron became coated with a thin film of oxide after water had been distilled on to it about twenty times and evaporated off again. The film, however, was confined entirely to

the surface of the iron, and none could be observed on the silica boat. This fact is an indication that the oxide was not deposited from solution, but was actually formed on the surface of the iron. This is no doubt due to the presence of a trace of oxygen. Minute quantities of air were probably retained by the baryta crystals. The crystals break up to an amorphous powder on repeatedly heating, and would thus allow of the escape of any air which had been occluded or enclosed. Most soluble crystalline substances disengage air when dissolved in water in a vacuum. The conditions of this experiment ensure the complete absence of carbon dioxide, but not of oxygen.

Tilden also calls attention to the fact that ferrous hydroxide is the first product in the rusting of iron. The following experiment also leads to the same conclusion which has been accepted in the previous papers.

A strip of iron was dropped into boiling water contained in a round Jena-glass flask. After continuing the boiling for a few minutes the flask was sealed and allowed to cool. When cold, air free from carbon dioxide was admitted. There was no change visible for about an hour, and then a white cloudiness began to form on the surface of the iron. This was evidently finely divided ferrous hydroxide; it was rapidly carried away from the iron by convection currents forming white streams in the water. This ferrous hydroxide was obviously formed at the surface of the iron, and afterwards carried out into the water. It did not make its appearance until the air had diffused down from the surface of the water and reached the iron. It was obviously extremely finely divided, being carried about by convection currents very readily. It was not for some hours that the ordinary yellow colour of rust made its appearance.

#### *The Cause of the Action of the Inhibiting Agents.*

As previously pointed out, any complete theory of rusting must include an explanation of the action of those substances which inhibit the process. During the course of this investigation it was found that, in addition to chromic acid and the chromates, many other agents also rendered iron passive, amongst them the alkalis. It was eventually found that all agents which inhibit rusting also render iron passive, and, further, that the inhibition of rusting is a direct result of the passive condition of the iron.

The following were the tests employed for showing the passivity of the iron:

- (1) A solution of nitric acid of specific gravity 1.2.

(2) A dilute solution of copper sulphate. A strength of 0.5 per cent. was found to be the most suitable.

(3) Immersion of the iron in distilled water, and observation of the time elapsing before rusting begins.

Of these tests the copper sulphate solution proved to be the most convenient.

With regard to the method of testing employed, some precautions are necessary in washing the iron and immersing it in the testing liquid. It must be washed with distilled water, and must not be touched with the hands or shaken too violently, since such action tends to destroy passivity. Perhaps the best method is to remove the iron from the solution by means of a very thin glass rod, bent into a hook at one end. The hook is inserted in a hole previously bored in the sheet of iron. The iron is quickly dipped two or three times in distilled water, and then immersed in the testing liquid and the rod removed.

A simpler method is to pour off the solution, and rinse out the vessel (a gas-jar is the most convenient) several times with distilled water. The testing liquid is then quickly poured over the iron so as completely to cover it. The whole process should be done as rapidly as possible, and without unduly shaking the iron.

Nitric acid of specific gravity 1.2 attacks active iron at once with effervescence and the formation of a brown solution. Passive iron is not so attacked, and will remain perfectly bright and unacted on for times varying from a few seconds to several hours. It is at once attacked, however, if touched with a piece of active iron or scratched with a sharp glass rod. The action visibly spreads from the point so touched over the whole surface.

Copper sulphate solution (0.5 per cent.) at once deposits a film of copper on active iron. Passive iron will remain in the solution sometimes for hours quite unaffected and perfectly bright. It becomes active, however, if touched with a piece of active iron or scratched with a glass rod, and the film of copper can be seen spreading from the point over the entire surface.

In distilled water exposed to the atmosphere, active iron usually begins to rust visibly in eight to ten minutes. Passive iron will sometimes remain perfectly bright for one to two hours before rusting begins, and then the action is very local for a considerable time. The most uniform results are given with iron which has been etched with nitric acid (D 1.2).

*Passivity induced by Agents which Inhibit Rusting.*

*Chromic Acid*:—Various strengths of chromic acid were employed, and the duration of the immersion was usually from eighteen hours to several days.

It was found that 1, 0·5, 0·1, 0·05, and 0·025 per cent. solutions of chromic anhydride rendered iron passive to nitric acid (D 1·2), the weaker solutions requiring a longer immersion up to four or five days. After prolonged immersion, iron was rendered slightly passive, even by a 0·01 per cent. solution of chromium trioxide. Iron which had been treated with 1 per cent. chromium trioxide remained passive to nitric acid (D 1·2) for several hours. In copper sulphate solution, iron which had been immersed in 1 per cent. chromium trioxide overnight remained unacted on for five hours. In distilled water exposed to the atmosphere, iron which had been immersed in 1 per cent. chromium trioxide for one day remained unattacked for considerable periods varying from one to two hours, and sometimes more. Rusting was only very local after four hours. In the blank test with active iron in distilled water, rusting began in ten minutes, and was copious in fifteen minutes.

The chromic acid used in these experiments was specially purified, and no sulphuric acid or nitric acid could be detected in it.

*One per cent. Solution of Potassium Dichromate*:—Pieces of iron, some with etched and some with unetched surfaces, were immersed in 1 per cent. dichromate for several days. On testing with nitric acid (D 1·2) they remained unattacked for times varying from a few seconds to several minutes.

Iron which had been immersed in 1 per cent. dichromate for two days was passive to 0·5 per cent. copper sulphate solution for twelve minutes. Iron was immersed for one day in 1 per cent. dichromate; it was then washed, and left in distilled water. There was no rusting after one and a-half hours, and only local rusting in four hours.

*One per cent. Solution of Potassium Chromate*:—Sheets of iron with etched surfaces were immersed in 1 per cent. potassium chromate for several days. They were then tested with nitric acid (D 1·2), and found to be passive for times varying from one minute to a few seconds.

Immersion for several days in 1 per cent. potassium chromate rendered iron passive to 0·5 per cent. copper sulphate solution, in which it remained unacted on for five hours.

Iron which had been treated with 1 per cent. potassium chromate for one day was immersed in distilled water, and showed no rusting for more than an hour.

*Potassium Chlorate*.—In a 1 per cent. solution iron rusted readily, and it remained active, as shown by all the three tests. In a 4 per cent. solution there was no rusting, and after a two days' immersion the iron was found to be passive to nitric acid (D 1·2) and to 0·5 per cent. copper sulphate. In distilled water, however, rusting began almost as quickly as in a blank test with active iron.

*Potassium Bromate*.—A 1 per cent. solution allowed slight incipient rusting. This soon stopped, and most of the surface remained bright. On testing the iron with nitric acid (D 1·2) (after an immersion of one day in the potassium bromate) it was found to be passive.

Another sheet of iron which had been immersed for two days in 1 per cent. potassium bromate was passive to 0·5 per cent. copper sulphate, and remained so for five minutes.

After treatment with the potassium bromate solution for one day a sheet of iron showed slight local oxidation. On washing and immersing in distilled water no additional rusting had occurred after one and three-quarter hours, and only very little in four hours.

*Potassium Iodate*.—In a 1 per cent. solution iron usually remained unruled. Several sheets of iron were treated for one or two days, and were then tested for passivity. One sheet was unacted on by nitric acid (D 1·2), another remained unacted on by 0·5 per cent. copper sulphate solution for three minutes, and a third on washing and immersing in distilled water did not begin to rust for fifty minutes.

*Potassium Permanganate*.—A sheet of iron which had been lying in 0·5 per cent. potassium permanganate solution for several weeks showed no rusting, although it had assumed a yellow colour owing to a thin film of manganese dioxide which had formed on it. On washing and immersing in nitric acid (D 1·2) the film of manganese dioxide was dissolved away, leaving the bright surface of the iron exposed. The iron remained unacted on for several hours, and was therefore passive.

*Sodium Arsenate*.—A 1 per cent. solution allowed a little local rusting to occur. This soon stopped, and most of the surface remained bright. On immersing in nitric acid (D 1·2) the green patch of rust slowly dissolved, leaving the bright iron surface quite unacted on.

*Hydrogen Peroxide*.—In a 1 per cent. solution (made from "Perhydrol," and quite free from acid) a smooth sheet of iron did not rust at all, but oxygen was continuously disengaged at the

surface of the iron. After immersion in the hydrogen peroxide solution for two days the iron was passive to nitric acid (D 1·2).

*Potassium Hydroxide*:—After immersion in 1 per cent. potassium hydroxide for twelve hours iron was found to be passive to nitric acid (D 1·2). Another sheet of iron, similarly treated, was passive to 0·5 per cent. copper sulphate solution, and remained unacted on for five hours.

Bright sheets of iron which had been immersed in 1 per cent. potassium hydroxide for one or two days did not begin rusting in distilled water for times varying from half an hour to one hour. In a blank experiment iron began to rust copiously in eight minutes.

*Barium Hydroxide*:—A solution of 1 per cent. baryta had the same effect as 1 per cent. potassium hydroxide.

*Sodium Carbonate*:—After being immersed for eighteen hours in 1 per cent. sodium carbonate the iron was passive to nitric acid (D 1·2). Also iron which had been kept for four months in solutions of 0·14 and 0·13 per cent. sodium carbonate and of 0·2, 0·15, and 0·14 per cent. potassium carbonate and had remained quite bright, was in every case passive to nitric acid (D 1·2).

After an immersion of eighteen hours in 1 per cent. sodium carbonate, iron was passive to copper sulphate solution, remaining unacted on for five hours.

Iron was treated with 1 per cent. sodium carbonate for three days, then washed thoroughly, and immersed in distilled water. Rusting did not begin for forty-five minutes. On repeating the experiment, rusting began very locally in half an hour. Blank tests were made at the same time, in which the active iron showed general rusting in eight minutes.

*Borax*:—After immersion overnight in 1 per cent. borax solution, iron was passive to nitric acid (D 1·2) for one minute. Another piece of iron which had been immersed in 1 per cent. borax for two days was passive to copper sulphate solution for five minutes. Iron with an etched surface was immersed in 1 per cent. borax for three days. It was then washed, and left in distilled water. No rusting was visible for an hour and a-half. A similar piece of active iron showed rusting in ten minutes.

*Ammonia*:—After immersion for two days in ammonia solution (D 0·880) iron was passive to nitric acid (D 1·2) for half a minute. Another piece of iron similarly treated was passive to copper sulphate solution, no action taking place for ten minutes.

*Potassium Ferrocyanide*:—Strips of iron were immersed in 1 per cent. potassium ferrocyanide solution for one day.

One piece on testing with nitric acid (D 1.2) was found to be passive. Another piece was tested with copper sulphate solution, and remained unacted on for one minute. A third piece was immersed in distilled water after carefully washing it. Rusting began very locally in half an hour, and there was still very little after an hour. A blank test showed general rusting in eight minutes.

Reference to the following table will show that in the case of solutions which do not inhibit the rusting of iron, such as sodium chloride, sodium sulphate, etc., no passivity of the iron was induced.

*Tabulated Results of Experiments on the Production of Passivity by Various Solutions.*

Solution.	Strength. Per cent.	Resulting state of iron in :			Whether solution inhibits or allows rusting.
		Nitric acid (D 1.2)	0.5 per cent. $\text{CuSO}_4$	Distilled water.	
Chromic acid	0.01 to 1	Passive	Passive	Passive	Inhibits
Potassium dichromate	1	Passive	Passive	Passive	Inhibits
Potassium chromate	1	Passive	Passive	Passive	Inhibits
Potassium chlorate	1	Active	Active	Active	Allows
Potassium bromate	1	Passive	Passive	Passive	Passive
Potassium iodate	1	Passive	Passive	Passive	Inhibits
Potassium permanganate	0.5	Passive			Inhibits
Sodium arsenate	1	Passive			Inhibits after slight initial action
Hydrogen peroxide	1	Passive			Inhibits
Potassium hydroxide	1	Passive	Passive	Passive	Inhibits
Barium hydroxide	1	Passive	Passive	Passive	Inhibits
Sodium carbonate	1	Passive	Passive	Passive	Inhibits
Sodium carbonate	0.13	Passive			Inhibits
Potassium carbonate	0.14	Passive			Inhibits
Borax	1	Passive	Passive	Passive	Inhibits
Ammonia	D 0.880	Passive	Passive		Inhibits
Sodium chloride	1	Active	Active	Active	Allows
Sodium sulphate	1	Active	Active	Active	Allows
Potassium nitrate	2	Active	Active		Allows
Potassium iodide	1	Active	Active		Allows
Potassium chlorate	4	Passive	Passive		Inhibits
Potassium ferrocyanide	1	Passive	Passive	Passive	Inhibits

From the above table it is evident that all those agents which inhibit rusting rendered iron passive, whilst those which allowed rusting did not render it passive. Not a single exception was found to this rule. The inference may therefore be drawn that the chromates, alkalis, and other inhibiting agents owe their action in preventing rusting to the fact that they all render iron passive to a greater or less extent.

That iron cannot rust so long as it is in the passive state was shown by the following experiment:

Four sheets of iron were immersed in 1 per cent. chromic acid for two days in separate vessels. They were thoroughly washed, and left to stand in distilled water. After one and a-half hours one of the pieces began to rust. It was tested with nitric acid (D 1·2), and found to be active. The other three which had remained perfectly bright were also tested, and found to be still passive to nitric acid (D 1·2). Thus, one of the pieces of iron had become active, and consequently rusted; the other three remained passive, and had therefore not rusted.

The fact that alkalis are capable, even when quite dilute, of rendering iron passive appears at first sight to be rather a startling one. But it has long been known that iron becomes passive in fused alkalis, and more recently several experimenters have shown that iron electrodes can be rendered passive in alkaline solution by passage of the electric current (P. Krassa, *Zeitsch. Elektrochem.*, 1909, 15, 490).

Two of the tests—the nitric acid (D 1·2) and the copper sulphate tests—showed that the alkalis act even more powerfully in this respect than potassium chromate and dichromate. In the case of the third test, namely, the rusting in distilled water, iron which had been rendered passive by alkalis did not appear to retain its passivity quite so long as iron similarly treated with the chromates. But when a control experiment with active iron is employed there can be no doubt whatever that the iron which has been treated with alkali has become passive, since it remains bright long after the iron used as the control has copiously rusted.

It should be added that dilute acids, including carbonic acid, as well as many salts, destroy more or less rapidly the passivity of iron. On any of the several theories as to the cause of the passivity of iron it is difficult to understand the passive effect induced by alkalis. It is not established that dilute alkaline solutions can induce the oxidation of iron and form a film of oxide on the surface. In fact, it is clear that the long-standing problem of the passivity of iron has not yet received complete explanation.

#### *Passivity and Rusting.*

The demonstration of the intimate connexion between the inhibition of the rusting of iron and its passivity renders a new theory of rusting necessary. The carbonic acid and the electrolytic theories depend largely on the fact that alkalis inhibit rusting; and since this phenomenon has now been explained in another way, these theories have lost the main support which justified their existence, besides being opposed to other facts alluded to above.

The fact that alkalis render iron passive negatives the conclusions



recorded in a paper published recently in support of the carbon dioxide or acid theory of rusting (Friend, *J. Iron Steel Inst.*, 1908, II, 5). In a series of experiments in which water was distilled on to iron in presence of air free from carbon dioxide, the iron was in some cases previously immersed in potassium hydroxide, and in others not. In all the experiments where the iron had been treated with potassium hydroxide it did not rust, but it did so when not previously so treated. The explanation given was that when the iron did not rust there was no carbon dioxide present; but when it did rust there was carbon dioxide present on the surface of the iron or glass, since these had not been immersed in potassium hydroxide. This is assumed to be so from the green colour of the rust characteristic of ferrous carbonate. The true explanation is that the iron did not rust because it had been rendered passive by the potassium hydroxide, whilst when not so rendered passive the iron did rust, in spite of the absence of carbon dioxide. The green colour of the rust was obviously the well-known colour of ferrous hydroxide containing a little ferric hydroxide.

Some of the results published by Moody in support of the carbonic acid theory now receive a different explanation. After treatment of iron with chromic acid and subsequent exposure to the action of water and air free from carbonic acid, the iron was found not to rust. The explanation is that it had been rendered passive by the chromic acid.

Iron which has been rendered passive by chromic acid will remain unruined in presence of water and air free from carbon dioxide for long periods. The access of carbon dioxide destroys the passivity, and rusting ensues.

It was pointed out previously in discussing the electrolytic theory that very dilute alkalis allow rusting to take place readily, although the concentration of the hydroxyl ions is overwhelmingly greater than that of the hydrogen ions of the water. According to the electrolytic theory this should not be so.

The phenomenon can, however, be very satisfactorily explained by the fact that alkalis below a certain dilution are not capable of rendering iron passive. Support is given to this view by some experiments which were carried out on the limiting concentration of alkalis just necessary to prevent rusting. It was found that 0.13 per cent. sodium carbonate and 0.14 per cent. potassium carbonate prevented rusting, and after immersion for four months the iron was found to be passive to nitric acid (D 1.2). With weaker solutions rusting occurred and the iron remained active. Similar results were obtained with dilute barium and sodium hydroxide solutions. An immersion of a few minutes in

the various reagents is often sufficient to effect the passivity of the iron.

*Comparison of the Oxidation of Iron with that of Other Metals.*

The respects in which the rusting of iron differs from the oxidation of other metals may now be considered. The following appear to be the principal differences:

(1) The rusting of iron is usually more continuous and deep-seated than that of most other metals; it produces pitting and a more rapid waste of the metal.

This has been ascribed to the fact that the oxides of the other metals are more coherent, and therefore more protective, than that of iron, and also to the fact that metallic iron is usually less pure than other metals, thus promoting electrolytic action. Lead is a good example of a metal which protects itself by means of a film of oxide. A bright surface of lead, however, begins to oxidise much sooner than a bright surface of iron. In distilled water lead shows visible oxidation in one or two minutes, whilst iron does not do so for seven or eight minutes. It therefore seems probable that this peculiarity of iron is not due to any fundamental difference in the chemical reaction of oxidation.

(2) The rusting of iron being inhibited by a large number of agents, the question arises as to whether other metals are similarly protected by all or some of these agents.

(3) Lastly, it is stated that hydrogen peroxide cannot be detected during the rusting of iron, whilst it can be detected during the rusting of other metals.

Apart from these three points the oxidation of iron does not appear to differ in any material way from that of other metals.

The table on p. 1850 summarises the results of experiments on the effect of various solutions on the oxidation of zinc, copper, aluminium, magnesium, and iron, and it may be added that the aerial oxidation of lead is inhibited by alkalis and by other of the agents mentioned which do not directly attack the metal.

It will be seen from this table that chromic acid inhibits metallic oxidation in all cases where the acid has no direct action on the metal. Potassium dichromate and chromate inhibit the oxidation of all the five metals. Sodium carbonate and borax inhibit the oxidation of iron, zinc, and copper, and allow an action in the case of aluminium and magnesium.

Potassium hydroxide appears to have a direct action on all the metals examined except iron. Potassium iodide allows oxidation of all the metals, and this is also the case with the chlorides, nitrates, and sulphates of the alkali metals, although they have

Solution.	Iron.	Zinc.	Copper.	Aluminium.	Magnesium.
Chromic acid	Inhibits	0.1% inhibits. 1% acts on the metal	Inhibits	Inhibits	Acts on the metal
Potassium di- chromate	Inhibits	Inhibits	Inhibits	Inhibits	Inhibits
Potassium chromate	Inhibits	Inhibits	Inhibits	Inhibits	Inhibits
Sodium car- bonate	Inhibits	2% inhibits. 1% allows some action	5% inhibits. Stronger solutions act on the metal	Acts on the metal with evolution of hydro- gen	Allows
Borax	Inhibits	1% inhibits	Inhibits	Retards	Allows
Potassium hydroxide	Inhibits	1% inhibits. Stronger solutions have a direct action	Allows	Acts on the metal with evolution of hydro- gen	Acts on the metal with evolution of hydro- gen
Potassium iodide	Allows	Allows	—	Allows	Allows
Potassium iodate	Inhibits	Allows	Acts on the metal pro- ducing blackening	Inhibits	Acts on the metal
Potassium bromate	Inhibits (after slight in- itial ac- tion).	Allows (acts on the metal)	—	—	—
Potassium ferrocyanide	Inhibits	Inhibits	Produces film on the metal	Inhibits	Allows
Potassium ferricyanide	Allows	Allows	Produces film on the metal	Allows	Allows

not been included on the list. Potassium iodate only inhibits in the case of iron and aluminium. Potassium ferrocyanide inhibits the oxidation of iron, zinc, and aluminium, whilst potassium ferricyanide allows an action with all the five metals.

It is thus evident that these various solutions exert an influence on the aerial oxidation of zinc, copper, aluminium, and magnesium very similar to that produced on the oxidation of iron. Especially is this true of the chromates. It has also been found that potassium bichromate and chromate render these metals passive just as they render iron passive.

*The Production of Hydrogen Peroxide during the Rusting of Iron.*

Direct proof that hydrogen peroxide is formed when iron rusts has not hitherto been available. Keiser and McMaster (*Amer. Chem. J.*, 1908, 39, 96), in testing for minute quantities of hydrogen peroxide, employed a mixture of potassium ferricyanide and ferric chloride solutions. They found this to be the most delicate reagent

of a large number which they tried. The potassium ferricyanide is acted on by hydrogen peroxide, giving ferrocyanide, which produces a coloration with the ferric chloride.

It was thought that this reagent might prove useful in testing for hydrogen peroxide during the oxidation of metals. On comparing its delicacy with that of titanio acid, it was found to be possible to detect hydrogen peroxide in a solution six times as dilute as one which just gave a yellow colour with titanio acid. The strength of these solutions was estimated, and it was concluded that one part of hydrogen peroxide in 200,000 parts of water could be detected by the ferricyanide reagent. A blank experiment must always be done at the same time, and the reagent must be freshly prepared and fairly dilute so as not to have too deep a colour.

This test was now applied to the oxidation of metals. The water in which zinc, lead, magnesium, and aluminium had been oxidising for a considerable time was tested. In every case the reagent turned green after remaining a short time, eventually becoming a very deep green and sometimes of a blue colour, thus showing the presence of hydrogen peroxide. Zinc and aluminium gave the strongest reactions.

Attention was now turned to iron. Some bright sheets of a highly purified soft iron were allowed to rust in distilled water, and the latter was tested from time to time for hydrogen peroxide. In order to make sure that no coloration of the reagent was caused by the presence of iron in solution, three parallel tests were employed; in addition to the actual test and the blank test with distilled water, a third test was made with ferricyanide to show whether there were any iron in solution. This last test almost invariably showed no coloration, and this showed that the results were not vitiated by the possible presence of iron in solution.

On the first day after the iron had been immersed no hydrogen peroxide could be detected in the water. On the second day, however, there was a slight reaction, and on the third day a pronounced reaction for hydrogen peroxide. Strong reactions continued to be given for about a fortnight, when they began to diminish, and eventually disappeared altogether. The strongest reactions obtained were quite comparable to those with lead and magnesium. On repetition of this experiment the same results were obtained, the presence of hydrogen peroxide usually lasting for a week or a fortnight, and finally disappearing. The eventual disappearance of the peroxide may be due to the formation of some ferrous hydroxide which would destroy it.

Thus in the case of iron a small quantity of hydrogen peroxide is formed during oxidation, just as with the other metals. The precise

significance of the formation of hydrogen peroxide during the aerial oxidation of metals has not yet been discovered.

### *Conclusions.*

None of the existing theories adequately explains how the various inhibiting agents prevent rusting. A satisfactory explanation, however, is provided by the fact that all these agents, without exception, render iron passive, and that this passivity persists after removal from the solution which caused it. Iron, so long as it is passive, does not rust in presence of oxygen and water. If exposed to atmospheric air, passive iron very gradually rusts, owing to the removal of the passivity of the iron by the carbon dioxide of the air. Passivity of metals may vary in amount, and the amount of rusting subsequently induced will depend on the extent to which this passivity is removed. The nature of passivity will be dealt with in another paper.

The mechanism of the process of the rusting of iron does not appear to differ essentially from the aerial oxidation of other metals. Similar reagents inhibit in all cases, and traces of hydrogen peroxide can be detected when iron rusts, just as in the case of the other metals. All the metals concerned will, however, readily oxidise in solutions of potassium iodide, and in certain other reducing agents which render the existence of hydrogen peroxide impossible. Consequently, the hydrogen peroxide is probably not an intermediate product of the main reaction, but may be the result of a secondary reaction, since the process of oxidation can apparently continue without its formation.

We consider, therefore, that metals undergo aerial oxidation by direct action of oxygen dissolved in water. In the case of iron, ferrous hydroxide is first produced, and is afterwards further oxidised to the ferric state, forming rust. Iron does not pass into solution before rust can be formed. The action of carbonic acid or of any other acid is separate and independent of the main process of rusting, which proceeds in their absence.

Several experiments which have been recently recorded as affording support to the old view that carbonic acid is necessary for the rusting of iron are explained by the results now recorded. The fact that iron which has been treated with dilute chromic acid or other inhibiting agents and subsequently washed, does not rust in air free from carbon dioxide, but begins to rust after carbon dioxide has been admitted, is due to the destruction of the passivity of the iron through the action of carbon dioxide.

A similar explanation can be given of an experiment recorded by Friend (*Proc.*, 1910, 26, 179), and intended as a lecture

experiment to demonstrate the necessity of carbonic acid for the rusting of iron. In this apparatus a hollow iron cylinder previously immersed in potassium hydroxide solution is shown afterwards not to rust in presence of water and air free from carbon dioxide. This result is due to the passivity of iron induced by the alkali, and does not prove, as is assumed, that iron cannot rust unless carbon dioxide is present. If carbon dioxide is admitted, the passivity of the iron is destroyed, and rusting proceeds (see also Dunstan, *Nature*, 1911, p. 331).

SCIENTIFIC DEPARTMENT,  
IMPERIAL INSTITUTE.

# CCIX.—*The Passivity of Iron and Certain Other Metals.*

By WYNDHAM ROWLAND DUNSTAN and JOHN RICHARD HILL.

THE evidence presented in the foregoing paper shows that the problems of passivity and the rusting of iron are closely connected. During the course of that investigation some new facts were brought to light which led to further experiments being made with regard to the passivity of both iron and other metals.

Of the numerous theories which have been put forward from time to time to explain the well known passive state of iron, not one can be said to have accounted successfully for all the observed phenomena. Most of these theories agree that passivity is caused by the formation of an extremely thin protective film on the surface of the metal. The protective film may possibly be composed of the metal itself, the surface of which has assumed some abnormal condition. Such a view is held by Hittorf, who considers that passivity is due to a state of electric tension on the surface of the metal (*Zeitsch. physikal. Chem.*, 1900, **34**, 385). Finkelstein expresses the opinion that the surface layer of the iron has been changed from the bivalent to the trivalent state (*Zeitsch. physikal. Chem.*, 1901, **39**, 91).

Then the protective film may also be of a non-metallic nature—either solid or gaseous. Fredenhagen believes it to be a film of oxygen in a condensed condition (*Zeitsch. physikal. Chem.*, 1903, **43**, 1; 1908, **63**, 1). Krassa (*Zeitsch. Elektrochem.*, 1909, **15**, 490) and many others adhere to the theory that passive iron is covered with a film of oxide—probably the magnetic oxide. This

is perhaps the theory which has received the most general support. Heathcote has summarised the facts at considerable length (*J. Soc. Chem. Ind.*, 1907, 26, 899), and draws the conclusion that none of the theories is satisfactory, but that the oxide theory has most in its favour. A similar view is held by Byers (*J. Amer. Chem. Soc.*, 1908, 30, 1718). The oxide film, if it exists, must be exceedingly thin, since it does not appear to affect the colour of the metal or to diminish its reflecting power. Müller and Königsberger (*Zeitsch. Elektrochem.*, 1907, 15, 659) performed experiments with iron mirrors, and could find no constant difference in the reflective power after rendering the iron passive. Krassa states that a film of oxide thick enough to produce passivity would not change the reflective power more than 2 per cent., and would therefore escape detection. Müller and Königsberger, however, deny this.

Krassa also gives an account of some work on the production of passivity of iron in alkali solutions by anodic polarisation. In boiling alkalis the passive state was quickly attained with strong currents, producing no visible alteration of the surface. With weak currents, however, a visible film of oxide was first produced, and this attained a considerable thickness before passivity was eventually arrived at. He attributed these results to the fact that with strong currents a complete, although thin, film of oxide was rapidly formed, whilst with weak currents the film was more irregular, and consequently attained a much greater thickness before becoming complete. Krassa considers that oxide is formed by direct electrolytic action of the alkali on iron with the liberation of hydrogen, the amount of hydrogen formed being usually too small to be detected.

It has been previously supposed that the passive state is confined to a very few metals, chiefly iron, nickel, and cobalt. It will be shown now, however, that other metals also exhibit passivity.

#### *The Passivity of Iron.*

As pointed out in the foregoing paper, all the solutions which inhibit rusting also render iron passive. The principal solutions are: chromic acid, potassium dichromate, chromate, permanganate, iodate, bromate, chlorate, and ferrocyanide, hydrogen peroxide, hydroxides of potassium, sodium, calcium, barium and ammonium, carbonates of sodium and potassium, and borax.

An immersion of a few minutes in one of these solutions is often sufficient to effect passivity. An account was given in the previous paper of the precautions to be taken in washing the iron and of the methods employed for detecting the passive state. The three tests were: nitric acid (D 1.2), a solution of copper sulphate (0.5 per cent.), and rusting in distilled water. As indicated in the fore-

going paper, the iron used in these experiments was wrought iron sheet of a high degree of purity, whilst sheet iron prepared by electrolysis furnished the same results.

#### *Influence of Air on Production of Passivity.*

That passivity is produced in the absence of air was shown in several ways:

(1) Iron was immersed in boiling 1 per cent. solutions of chromic acid, potassium dichromate, sodium carbonate, and potassium hydroxide for several hours. In every case the iron was found to be passive to nitric acid (D 1·2) after this treatment.

(2) Iron was dropped into a boiling 1 per cent. solution of sodium carbonate contained in a flask. The flask was sealed while boiling, and allowed to cool. After twenty-four hours the flask was opened, and the iron was found to be passive on testing with nitric acid (D 1·2). The experiment was also made with 1 per cent. solutions of chromic acid and potassium bromate, both of which gave the same result.

(3) Some iron was placed in one limb of a bent tube and a 3 per cent. solution of potassium hydroxide in the other. The tube was connected with a Sprengel pump and completely evacuated, the potassium hydroxide being finally boiled to drive out all dissolved air. The tube was then sealed, and the alkali run over on to the iron, where it was allowed to remain overnight. The alkali was then poured back again, and the iron washed repeatedly by distilling water over from the alkali. Finally, the tube was carefully opened, the iron tested with copper sulphate solution, and found to be passive.

Thus, in all these cases air plays no part in rendering iron passive.

#### *Destruction of Passivity.*

When iron which had been rendered passive by chromic acid was washed and immersed in distilled water, it usually remained passive for upwards of an hour. Eventually, however, it slowly became active, and rusting began. This action was due to the carbonic acid from the air which destroyed the passivity. This was shown to be so by an experiment in which carbon dioxide was rigorously excluded, and the iron protected from contact with the glass by means of a silica boat. In this case no rusting had occurred after several months. When the iron had not been previously rendered passive, rusting occurred as usual.

The passivity was not destroyed in distilled water by touching the iron with zinc or active iron. It was, however, thus destroyed



when immersed in copper sulphate solution or in nitric acid (D 1·2). In these solutions the action began at the point touched, and visibly spread over the surface; thus, when passive iron is immersed in electrolytes, the active state is able to spread rapidly from any active spot over the whole surface, whereas in distilled water activity spreads much more slowly. This was further shown by scratching the surface of passive iron. In nitric acid (D 1·2) and in copper sulphate solution action spreads rapidly from the scratch over the whole surface; in distilled water the rest of the surface remained passive for some time after the scratch had rusted.

Passivity was also destroyed by violently shaking the iron against the sides of the vessel or by touching with the fingers. Consequently, care must be exercised in washing and testing passive iron. Steel was found to behave in exactly the same way as wrought iron, except that it became active rather more readily.

*Dilute Acids Destroy the Passivity of Iron.*

(1) *Sulphuric Acid*:—Iron which had been rendered passive with 1 per cent. chromic acid was washed in distilled water, and immersed in dilute sulphuric acid of various strengths down to  $N/10$ . In all cases effervescence began in the course of some minutes, and on testing the iron with copper sulphate it was found to have become active.

(2) *Hydrochloric Acid*:— $N/10$ -Acid rendered passive iron active in less than half a minute.

(3) *Acetic Acid*:—Passive iron was immersed in 5 per cent. acetic acid. It became active in fifteen minutes. In 2 per cent. acid the iron became active in twenty minutes, whilst in 1 per cent. acid the passivity was not destroyed for over an hour.

(4) *Formic Acid*:—A 1 per cent. solution rendered passive iron active in five minutes.

(5) *Citric Acid*:—A 1 per cent. solution destroyed passivity in twelve minutes.

(6) *Carbonic Acid*:—When passive iron was immersed in solutions of carbon dioxide it became active in times varying from half to one hour, depending on the extent of the passivity and on the strength of the solution of carbonic acid.

Reducing agents do not destroy passivity.

Passive iron was washed in distilled water, and immersed in solutions of formaldehyde, ammoniacal cuprous oxide, sodium hypophosphite, and alkaline dextrose. In all cases the iron remained passive.

*Salt Solutions Destroy Passivity.*

It has been known for some time that the presence of sodium chloride and other haloid salts prevents iron from attaining the passive state.

A sheet of passive iron was immersed in a 2 per cent. solution of sodium chloride. Rusting began in seven or eight minutes, which is also the time required for active iron to rust. Other sheets of passive iron were immersed in 2 per cent. sodium chloride for one minute and half a minute respectively. They were then tested with nitric acid (D 1.2), and found to be active. Solutions as dilute as 0.005 per cent. of sodium chloride gave similar results. Various other chlorides were employed, and all had the same vivifying effect. These were the chlorides of potassium, calcium, chromium, iron, and ammonium. Bromides and iodides were also found to destroy passivity. Other salts were then tried. Various nitrates and sulphates were found to destroy passivity, although not so rapidly as the haloid salts.

If any one of these salts is added to a solution which renders iron passive, the latter property should be nullified, and the iron remain active, and consequently rust. This was found to be actually the case. Sodium chloride was added to a solution of potassium chromate, and a piece of iron dropped in. Rusting readily occurred, although rather locally, and rapidly went deeply into the metal. The same result occurred when sodium chloride or one of the above-mentioned salts was added to a solution of sodium carbonate, potassium hydroxide, or hydrogen peroxide. Rusting occurred in every case. With chromic acid, the addition of sodium chloride caused a rapid action on iron, with reduction of the chromic acid and evolution of hydrogen. With potassium dichromate, which has a slightly acid reaction, the same result was obtained, except that there was less hydrogen produced.

The cause of the vivifying action of salts is elucidated by the results of the following experiments:

A sheet of iron was immersed in a solution of sodium chloride containing a few drops of phenolphthalein. A pink colour was rapidly developed on certain areas of the surface of the metal, indicating the formation of free alkali. It was found that the same effect was produced by other salts of the alkali metals, and was evidently caused by a difference of potential being set up, which resulted in slight electrolysis of the salt. In order to ascertain whether the difference of potential was set up by the oxidising action of the air on the iron, the experiment was repeated with complete exclusion of air. In this case no pink colour was formed.

Air was then admitted, and as soon as it had diffused down to the iron, the pink colour appeared in patches as before, rusting occurring on the areas which were not coloured. It is obvious, therefore, that the difference of potential is due to the irregular action of the air on the iron, since it does not occur in absence of air.

These experiments were now repeated, using passive instead of active iron. Exactly the same phenomena were observed, showing that in the presence of sodium chloride the action of the air can also set up a difference of potential on passive iron.

As a consequence of these experiments it may be said that the vivifying effect of salts is due to an electrolytic effect. This is caused by a difference of potential set up on the surface of the iron by the action of the air, which causes the liberation of alkali from the salt at the cathodic portions, and of the acid radicle at the anodic portions. It is the latter which acts on the outer film of the iron, and destroys the passivity.

If this explanation is correct, salt solutions should not destroy the passivity of iron in absence of air, since no difference of potential

FIG. 1.



would then be set up. This was shown to be actually the case by the following experiment.

A bent glass tube *A B* was taken, and the end *B* drawn out to a fine capillary. A strip of dry passive iron (see below) was placed in the tube at the end *A*, which was then drawn out as shown. A 1 per cent. solution of sodium chloride was drawn in at *B*, and the capillary sealed. The end *A* was connected to a Sprengel pump, and the tube was completely evacuated, the solution being finally boiled to expel all air. The tube was then sealed at *A*, care being taken that no salt solution should touch the iron. The solution was now poured over on to the iron, allowed to remain there for half an hour, and then poured back again. The iron was washed free from sodium chloride by carefully distilling water over from *B* several times, keeping the limb *A* cool. Finally, the tube was opened, and the iron carefully transferred to a vessel containing copper sulphate solution, when it was found to be passive. Care was taken throughout not to shake the iron unduly. The experiment shows that in absence of air sodium chloride does

not destroy the passivity of iron. The strong vivifying effect is due to the combined action of both air and sodium chloride.

*The Film Theory of Passivity.*

The following experiments were made in order to gain further information respecting the production of a film as a probable cause of passivity:

Two polished sheets of iron, *A* and *B*, were taken. *A* was scratched with a sharp glass rod, and both were then immersed in a 1 per cent. solution of potassium dichromate overnight in separate vessels. On the following morning they were washed, and immersed in distilled water. The sheet *B* was then scratched. In eight to ten minutes the scratch on *B* began to show rusting, and after forty-five minutes was completely covered with rust, the rest of the surface remaining quite bright. The sheet *A* was entirely free from rust. This experiment shows that if the surface of iron is scratched after it has been rendered passive, active iron is exposed at the part scratched.

Similar results were obtained in other experiments. A sheet of iron was rendered passive in chromic acid. It was then washed in distilled water, and immersed in nitric acid (D 1.2). No action took place. The metal was now scratched with a sharp glass rod, when vigorous action at once set in at the scratch, and rapidly spread over the whole surface. On repeating the experiment in a copper sulphate solution, a similar result was obtained. Copper was at once deposited on the scratch, and the action rapidly spread outwards over the rest of the surface.

These experiments clearly indicate the presence of some kind of protective film on the surface of the passive iron. When a portion of this film is removed or disturbed, the original metal is thereby exposed, and the part so treated is rendered active. Violent shaking of the iron also may injure the film and cause activity.

That the film is not gaseous or in any way volatile was shown by the following experiments:

Several sheets of iron which had been rendered passive in chromic acid were obtained in the dry state, by washing first in distilled water and then in alcohol, and finally drying in a rapid current of air. The sheets so treated were found to retain their passivity for long periods in the dry state.

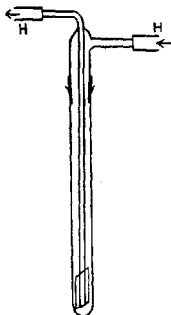
One of the sheets of dry passive iron was heated at 100° in a steam-oven for several hours, and was still passive. Another sheet was placed in a tube sealed at one end, which was then connected to a Sprengel pump and evacuated. It was heated at 100° for an

hour, when the iron was tested with copper sulphate solution, and found to be passive.

Higher temperatures were now employed, great care being taken to obtain a complete vacuum. Combustion tubing was used, and it was heated in a bath of soft solder (melting point  $184^{\circ}$ ), the temperature being measured with a thermometer reading to  $500^{\circ}$ . In this way a sheet of passive iron was heated in a vacuum at  $350^{\circ}$  for fifteen minutes. After allowing to cool, the iron was tested with copper sulphate solution, when it was found to be passive. The experiment was repeated at higher and higher temperatures, and it was found that iron remained passive in a vacuum up to  $400^{\circ}$ . When the temperature was raised above  $400^{\circ}$  the passivity gradually disappeared.

Passive iron was heated in a sealed combustion tube, through which a current of hydrogen was passed, thus:

FIG. 2.



The hydrogen was dried, and passed over a heated copper spiral before entering the tube, so as to exclude all traces of oxygen. The tube was heated in a sulphuric acid bath at the lower temperatures, and in a solder-bath at the higher temperatures. The iron was tested at the end of each experiment with copper sulphate solution.

After heating at  $200^{\circ}$  for 15 minutes, the iron was passive.

"	220	"	"	"
"	240	"	"	"
"	250	"	"	active
"	300	"	"	"
"	350	"	"	"

Thus the passivity of iron was destroyed by heating in hydrogen between  $240^{\circ}$  and  $250^{\circ}$ .

## THE PASSIVITY OF IRON AND CERTAIN OTHER METALS. 1861

Parallel experiments were done, in which passive iron was heated in nitrogen. They gave the same results as heating in a vacuum, namely, the passivity was not destroyed below  $400^{\circ}$ .

The temperature at which passivity was destroyed in hydrogen is evidently the same as the temperature at which the magnetic oxide begins to be reduced when heated in hydrogen.

This was further shown to be the case by the following experiment: A sheet of iron was coated with an extremely thin film of oxide by carefully heating in air or steam until it had assumed a slight orange colour. It was then heated in a current of hydrogen. Between  $240^{\circ}$  and  $250^{\circ}$  the oxide film was reduced, and disappeared.

These results afford strong evidence in favour of the probable existence of a film of oxide on the surface of passive iron.

### *The Passivity of Zinc.*

In the case of zinc the passive state was shown by means of the same tests as those employed with iron.

(1) *Copper Sulphate Solution*:—Ordinary zinc, which is in the active state, is immediately attacked by a dilute solution of copper sulphate (0.5 per cent.), a dark layer of copper being at once deposited. In the passive state, however, zinc remains quite bright in copper sulphate solution for several minutes, and then a furry deposit of copper slowly begins to form.

(2) *Oxidation in Distilled Water*:—A bright sheet of active zinc begins to show oxidation in distilled water in fifteen minutes, and after one or two hours the oxidation has become general. Passive zinc, on the other hand, shows no oxidation in distilled water for many days, and often for several weeks.

### *Agents which Render Zinc Passive.*

A solution of potassium dichromate was found to be the best agent for rendering zinc passive. Bright sheets of zinc were immersed in a 1 per cent. solution of potassium dichromate overnight. Being quite bright they were washed, and tested by the above methods. They were quite passive, both to copper sulphate solution and aerial oxidation in distilled water.

Solutions of chromic acid between 0.01 and 0.1 per cent. were also found to render zinc passive to both tests. A 1 per cent. solution, however, acted on the metal, with the formation of a layer of chromate. A 1 per cent. solution of potassium chromate rendered zinc passive towards copper sulphate solution, and towards oxidation in distilled water, although not so completely as did potassium

dichromate. Two per cent. solutions of sodium carbonate and of borax also rendered zinc partly passive. Stronger solutions had a direct action on the metal, which was also the case with potassium hydroxide and other strong alkalis.

*Effect of Scratching the Surface of Passive Zinc.*

A sheet of zinc which had been rendered passive in potassium dichromate was washed in distilled water, and scratched with a sharp glass rod. On immersing in copper sulphate solution, the scratch was immediately blackened by deposition of copper, the rest of the surface remaining bright for some time. When active zinc was treated in the same way, the scratch made no difference, the whole surface being immediately blackened. Another sheet of passive zinc was immersed in distilled water, and scratched as before. Oxidation rapidly began on the scratch, and after several days this was completely oxidised; the rest of the surface remained bright for a week or two.

These experiments afford strong evidence of a protective film on the surface of passive zinc, as was found in the case of iron.

The passivity of zinc is not destroyed by the action of dissolved air nearly so readily as that of iron. This is shown by its remaining unoxidised in distilled water for much longer periods. Also, salt solutions do not vivify passive zinc so readily as they do passive iron.

On the other hand, however, zinc largely loses its passivity on washing with alcohol, and drying. Consequently, some experiments in which dry passive zinc was heated in hydrogen were not found to be of much value in determining the nature of the protective film. Also, zinc oxide is not reduced by heating in hydrogen until after the melting point of the metal is reached.

*The Passivity of Magnesium.*

Magnesium will remain unoxidised for long periods if previously immersed in solutions of potassium dichromate or chromate. This is due to the fact that these reagents render it passive, as the following experiments show.

A sheet of magnesium was immersed for forty-eight hours in a 1 per cent. solution of potassium dichromate. It was then washed, and immersed in distilled water. A sheet of ordinary magnesium was also immersed in distilled water at the same time. The surface of the latter was almost immediately covered with bubbles of hydrogen, and in ten minutes visible oxidation had begun. The passive magnesium remained unchanged, and no gas was formed for

half an hour. The active magnesium then showed general oxidation over the whole surface. In two hours the passive sheet was quite bright, but showed slight effervescence. After twenty-four hours it was still bright; general oxidation had set in after 'forty-eight hours' immersion.

A similar experiment was performed, using a 1 per cent. solution of potassium chromate instead of dichromate. The passive magnesium only showed slight effervescence after half an hour, and remained bright for twenty-four hours, when general oxidation set in. The active metal began to oxidise in ten minutes as before.

Chromic acid has a direct action on magnesium, the surface of the metal becoming tarnished.

#### *The Passivity of Copper.*

Copper is rendered passive by immersion in solutions of chromic acid, potassium dichromate, and potassium chromate. Potassium hydroxide does not render copper passive, nor does it inhibit oxidation of the metal. The passive condition was shown by the following experiments:

(1) A sheet of pure copper was immersed in a 1 per cent. solution of potassium dichromate for about twelve hours. It was then washed, and immersed in distilled water. A similar sheet of active copper was also immersed in distilled water at the same time. The latter showed oxidation in the form of a thin film after three days. After a week the surface was much discoloured. The passive copper, on the other hand, had remained perfectly bright. After three weeks the surface of the active copper was completely oxidised, that of the passive copper being quite bright, and remaining so for over a month.

(2) Two sheets of copper, one of which had been immersed overnight in a 1 per cent. solution of potassium dichromate, were placed in separate vessels. A 0.1 per cent. solution of silver nitrate was poured over both. The active copper was at once acted on, being covered with a steely-blue film of silver. The passive copper remained unchanged for three or four minutes, and then a furry, grey deposit of silver slowly began to form.

(3) The previous experiment was repeated, using a dilute solution of mercurous nitrate instead of silver nitrate. Similar results were obtained.

(4) A dilute solution of silver acetate caused a deposit of silver on active copper in a few seconds. Passive copper was not acted on for more than half an hour.



*Cause of the Passivity of Copper.*

(1) Some passive copper was washed, and immersed in distilled water. It was then scratched with a sharp glass rod. In two days the scratch had begun to oxidise, and after a week was completely coloured dark red or black, the rest of the surface remaining perfectly bright. A piece of active copper was treated in the same way, but the scratch made practically no difference, and general oxidation began in the usual way in a few hours.

(2) A sheet of passive copper was scratched, and immersed in silver nitrate solution. The scratch was immediately blackened by deposition of silver, the rest of the surface remaining unchanged for some time. When active copper was treated in the same way, the whole surface was immediately blackened. The experiment was repeated with silver acetate with the same results.

(3) A sheet of copper was carefully polished with fine emery, and immersed overnight in a 5 per cent. solution of potassium dichromate. It was then washed, and carefully dried with a soft cloth. One-half of the surface was now polished up again with the same emery as before, care being taken throughout not to touch the metal with the fingers. On comparing the two portions, it was observed that the one not so recently polished was of a slightly redder colour than the other. The sheet was now immersed in distilled water in a covered gas-jar, and left to remain. In three days general oxidation had begun on the more recently polished portion, the rest of the surface being unchanged. After ten days the active portion had oxidised copiously, the rest of the surface remaining perfectly bright.

These experiments show that passive copper is covered with a protective film, and that the colour of the metal is rendered slightly redder in consequence.

In order to ascertain whether the film on passive copper is non-metallic, the rate at which passive copper amalgamates with mercury was compared with that of active copper. Two sheets of copper, one active and the other passive, were pressed down into mercury by means of glass rods hooked at the end, and the whole covered with distilled water. In fifteen minutes the active copper showed distinct amalgamation, whereas the passive copper did not begin to amalgamate for several hours, and even then only slowly. It is therefore improbable that the protective film consists of metal in an abnormal physical condition, and the evidence points to the conclusion that it is an oxide.

To show whether copper is oxidised by the action of chromates, a sheet of the metal was immersed in a solution of potassium chromate

to which ammonia had been added. A rapid action took place, copper passing into solution, and the chromate being reduced. Ammonia solution by itself has a much slower solvent action on copper, due to the oxidising action of the air. In both cases the oxide is dissolved by the ammonia as rapidly as it is formed. In this way the oxidising action of the chromate is rendered continuous by the constant exposure of a fresh surface of the metal.

The same result was obtained by the addition of dilute sulphuric or hydrochloric acid instead of ammonia. In this case the acid dissolves the film of oxide; thus, the copper passes into solution, and the chromate is reduced.

These results afford strong evidence that chromic acid and the chromates render copper passive by the production of a film of oxide on the surface of the metal.

Support for this view was also obtained by the action of the following solutions on passive copper:

*Sulphuric Acid*:—Passive copper was immersed in sulphuric acid of various dilutions down to  $N/50$ . In all cases the passivity was destroyed within two or three minutes.

*Hydrochloric Acid*:—Passive copper was treated with  $N/50$  hydrochloric acid. On testing with silver acetate solution it was found to have become active.

*Ferrous Sulphate*:—On treating passive copper with a solution of ferrous sulphate, it was rendered active. A solution of ferrous sulphate dissolves copper oxide, with formation of ferric hydroxide.

*Citric Acid*.—A 10 per cent. solution rendered passive copper active.

These four reagents all dissolve copper oxide, and they all render passive copper active. Other acids which dissolve copper oxide also destroy the passivity of copper.

Copper rapidly loses its passivity when dried by washing in alcohol, and it is known that finely divided cuprous oxide is rapidly reduced by alcohol.

#### *The Passivity of Lead.*

Lead appears to behave similarly to copper and zinc, but the action in this case was not minutely studied.

#### *Conclusions.*

The results of this investigation leave little room for doubt that the observed passivity is due to the presence of a film of oxide on the surface of each metal. With iron this film remains intact on heating in a vacuum to temperatures as high as  $400^{\circ}$ . It cannot therefore be composed of a gas film. The film is, however, destroyed

by heating in hydrogen at  $250^{\circ}$ , the temperature at which magnetic iron oxide begins to be reduced. This is strong evidence in favour of the film being composed of an oxide of iron, and this explanation is supported by the fact that many dilute acids which dissolve the oxides of iron also destroy passivity. It is more difficult, however, to explain the action of the alkalis on this basis. It is known, however, that under certain conditions iron can be oxidised by alkalis with the production of a visible film of oxide. Presumably such oxidation can only take place with the liberation of hydrogen, and it has not so far been recognised that iron can react with cold dilute alkalis.

The strong vivifying effect of salt solutions, and especially of the haloid salts, is shown to be due to an electrolytic action, in which the acidic ion is liberated and attacks the film.

Zinc, copper, and magnesium can also assume the passive state. The passivity of zinc and copper is to be attributed to the formation of a protective film, which, in the case of copper, causes the metal to assume a slightly redder colour. The film is non-metallic, since it interferes with the amalgamation of copper by mercury.

The passivity of copper is destroyed by various reagents which dissolve the oxides of copper. Also, chromic acid and the chromates have been shown to exert an oxidising action on copper. It is therefore concluded that the passivity of copper is due to the formation of a film of oxide, probably cuprous oxide, on the surface of the metal. The cases of zinc, lead, and magnesium are no doubt also to be explained by the formation of films of the oxides of these metals.

SCIENTIFIC DEPARTMENT,  
IMPERIAL INSTITUTE.

INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS, 1912. 1867

The Council has ordered the following letter and report to be printed in the Journal and Proceedings of the Society:

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,  
ROYAL COLLEGE OF SCIENCE,  
SOUTH KENSINGTON,  
LONDON, S.W.  
October 4th, 1911.

GENTLEMEN,

I beg to forward you the Annual Report of the International Committee on Atomic Weights for 1912, to which I have appended, as desired by them, the signatures of Professors Clarke, Ostwald, and Urbain.

Slight changes have been made in the atomic weights of calcium, erbium, iron, mercury, tantalum, and vanadium, which are indicated, in accordance with a suggestion received from Germany, by asterisks.

The only addition to the list of elements is that of niton (radium emanation), with the symbol Nt, and the atomic weight 222.4, as determined by Gray and Ramsay. This is in fair agreement with the value calculated by Debierne from observations on the rate of flow of the gas.

I have the honour to be, Gentlemen,  
Your obedient servant,  
T. E. THORPE.

To the Hon. Secretaries,  
The Chemical Society,  
Burlington House,  
London, W.

Report of the International Committee on Atomic Weights, 1912.

Since the report of the Committee for 1911 was prepared, a number of important determinations of atomic weight have been published, which may be summarised as follows:

*Nitrogen*.—Guye and Drouguine (*J. Chim. Phys.*, 1910, **8**, 473), from seven analyses of  $N_2O_4$ , find, in mean,  $N=14.010$ .

*Sulphur*.—Burt and Usher (*Proc. Roy. Soc.*, 1911, **A**, **85**, 82), by analysis of nitrogen sulphide,  $N_4S_4$ , have determined the ratios  $S:N::1.0:0.43687$ . Hence, calculating with  $N=14.009$ ,  $S=32.067$ , in good agreement with the accepted value.

*Chlorine*.—Burt and Gray (*Chem. News*, 1911, **103**, 161 and 170) have continued their work upon the density of hydrochloric acid, and confirmed their former determination of  $Cl=35.46$ .

**Iodine.**—Baxter (*J. Amer. Chem. Soc.*, 1910, **32**, 1591) has re-determined the ratio of iodine to silver with extreme care. Combining his results with the previously-determined ratio of silver to iodine pentoxide, he finds  $\text{Ag}=107.864$  and  $\text{I}=126.913$ . The value for silver varies from that found by Richards and Willard, and the discrepancy is as yet unexplained.

**Sodium.**—Goldbaum (*J. Amer. Chem. Soc.*, 1911, **33**, 35) has made analyses of sodium chloride and bromide by a new electrolytic method. The salts were electrolysed with a mercury anode and a weighed silver cathode, and on the latter the halogen was collected in weighable form. From the chloride, with  $\text{Cl}=35.458$ , Goldbaum found  $\text{Na}=22.997$ ; the bromide, with  $\text{Br}=79.920$ , gave  $\text{Na}=22.998$ .

**Calcium.**—Two papers by Richards and Hönigschmid (*J. Amer. Chem. Soc.*, 1910, **32**, 1577; 1911, **33**, 28) on the atomic weight of calcium have appeared. From analyses of calcium bromide,  $\text{Ca}=40.070$ , when  $\text{Ag}=107.88$ . From analyses of the chloride,  $\text{Ca}=40.074$ . The value 40.07 is adopted in the table at the end of this report.

**Cadmium.**—Perdue and Hulett (*J. Physical Chem.*, 1911, **15**, 155; see also Richards, *J. Amer. Chem. Soc.*, 1911, **33**, 888), from electrolytic analyses of cadmium sulphate, conclude that the atomic weight of cadmium is near 112.30. This is lower than the accepted value, but as the investigation is being continued with other salts of cadmium, any change in the table should be deferred.

**Mercury.**—Easley (*J. Amer. Chem. Soc.*, 1910, **32**, 1117) has continued his work on the atomic weight of mercury, varying his methods. New analyses of the chloride give  $\text{Hg}=200.63$ , in confirmation of his former determinations. In a private communication he states that analyses of the bromide lead to the same value. The new figure,  $\text{Hg}=200.6$ , should be adopted.

**Vanadium.**—McAdam (*J. Amer. Chem. Soc.*, 1910, **32**, 1603), by reducing sodium vanadate to sodium chloride, by heating in a stream of dry hydrochloric acid, finds  $\text{V}=50.967$ , or 51 in round numbers. The latter figure is as probable as any.

**Tantalum.**—Balke (*J. Amer. Chem. Soc.*, 1910, **32**, 1127), by hydrolysis of tantalum pentachloride, has determined the ratio  $2\text{TaCl}_5:\text{Ta}_2\text{O}_5$ . The mean of five concordant determinations gives  $\text{Ta}=181.52$ , when  $\text{Cl}=35.46$ . The rounded-off value 181.5 should be accepted.

**Tellurium.**—Flint (*Amer. J. Sci.*, 1910, [iv], **30**, 209) has continued the work reported by Browning and Flint in 1909 on the fractionation of tellurium by hydrolysis of the tetrachloride. With successive fractions the atomic weight steadily decreased. Seven analyses of the basic nitrate representing the tenth fractionation gave values for  $\text{Te}$  ranging from 124.25 to 124.42. As the work

is still in progress, any acceptance of these low figures would be premature.

*Iron*.—Baxter, Thorvaldson, and Cobb (*J. Amer. Chem. Soc.*, 1911, **33**, 319), from analyses of ferrous bromide, find  $\text{Fe}=55.838$  when  $\text{Ag}=107.88$ . In another communication (*ibid.*, p. 337), Baxter and Thorvaldson find  $\text{Fe}=55.836$ . The latter figure is the mean of two series, *meteoric* iron being taken as the starting point. The value  $55.84$  is given in the table.

*Uranium*.—Oechsner de Coninck (*Compt. rend.*, 1911, **152**, 711 and 1179), by reduction of  $\text{UO}_2\text{Cl}_2$  and  $\text{UO}_3\cdot\text{H}_2\text{O}$  to  $\text{UO}_2$  in hydrogen, concludes that  $\text{U}=238.5$ . The work is only approximate in character.

*Scandium*.—Meyer and Winter (*Zeitsch. anorg. Chem.*, 1910, **67**, 398), in a preliminary series of experiments, find values for Sc ranging from  $44.86$  to  $45.37$ ; in mean,  $45.12$ . This is higher than the recognised value, but its adoption would be premature. More details are needed.

*Neodymium*.—By extended and careful analyses of the chloride, Baxter and Chapin (*Proc. Amer. Acad.*, **46**, 215) have redetermined the atomic weight of neodymium. From the ratio  $\text{NdCl}_3:3\text{Ag}$ ,  $\text{Nd}=144.268$ . From the ratio  $\text{NdCl}_3:3\text{AgCl}$ ,  $\text{Nd}=144.272$ . A small correction raises the value to  $144.275$ . The rounded-off value  $144.3$ , given in the table, may be properly retained.

*Erbium*.—Hofmann (*Ber.*, 1910, **43**, 2635), from analyses and syntheses of the sulphate of "neocerium," finds  $\text{Er}=167.68$ . This may be rounded to  $167.7$ .

*Argon*.—Determinations of the density of argon, by Fischer and Froboese (*Ber.*, 1911, **44**, 92), give a mean value of  $19.95$ . Hence  $\text{A}=39.90$ .

*Niton*.—Gray and Ramsay (*Proc. Roy. Soc.*, 1910, **A**, **84**, 536), with the aid of the microbalance, have determined the density of the gaseous emanation from radium, to which they give the name *niton*. The mean value found gives  $\text{Nt}=223$ , but the value  $222.4$  is preferred (compare also Debierne, *Compt. rend.*, 1910, **150**, 1740). The gas is a member of the argon group, and seems to be entitled to recognition in the table.

The table of atomic weights for 1912 follows. In accordance with a suggestion received from Germany, the changed values are indicated by an asterisk. The changes are few in number, and only in two cases are they large.

F. W. CLARKE.  
W. OSTWALD.  
T. E. THORPE.  
G. URBAIN.

1912.

*International Atomic Weights.*

O=16.		O=16.	
Aluminium .....	Al 27.1	Molybdenum .....	Mo 96.0
Antimony .....	Sb 120.2	Neodymium .....	Nd 144.3
Argon .....	A 39.88	Neon .....	Ne 20.2
Arsenic .....	As 74.96	Nickel .....	Ni 58.68
Barium .....	Ba 137.37	Niton* (radium emanation) Nt	222.4
Bismuth .....	Bi 208.0	Nitrogen .....	N 14.01
Boron .....	B 11.0	Osmium .....	Os 190.9
Bromine .....	Br 79.92	Oxygen .....	O 16.00
Cadmium .....	Cd 112.40	Palladium .....	Pd 106.7
Cesium .....	Cs 132.81	Phosphorus .....	P 31.04
Calcium* .....	Ca 40.07	Platinum .....	Pt 195.2
Carbon .....	C 12.00	Potassium .....	K 39.10
Cerium .....	Ce 140.25	Praseodymium .....	Pr 140.6
Chlorine .....	Cl 35.46	Radium .....	Ra 226.4
Chromium .....	Cr 52.0	Rhodium .....	Rh 102.9
Cobalt .....	Co 58.97	Rubidium .....	Rb 85.45
Columbium .....	Cb 93.5	Ruthenium .....	Ru 101.7
Copper .....	Cu 63.57	Samarium .....	Sa 150.4
Dysprosium .....	Dy 162.5	Scandium .....	Sc 44.1
Erbium* .....	Er 167.7	Selenium .....	Se 79.2
Europium .....	Eu 152.0	Silicon .....	Si 28.3
Fluorine .....	F 19.0	Silver .....	Ag 107.88
Gadolinium .....	Gd 157.3	Sodium .....	Na 23.00
Gallium .....	Ga 69.9	Strontium .....	Sr 87.68
Germanium .....	Ge 72.5	Sulphur .....	S 32.07
Glucium .....	Gl 9.1	Tantalum* .....	Ta 181.5
Gold .....	Au 197.2	Tellurium .....	Te 127.5
Helium .....	He 3.99	Terbium .....	Tb 159.2
Hydrogen .....	H 1.008	Thallium .....	Tl 204.0
Indium .....	In 114.8	Thorium .....	Th 232.4
Iodine .....	I 126.92	Thulium .....	Tm 168.5
Iridium .....	Ir 193.1	Tin .....	Sn 119.0
Iron* .....	Fe 55.84	Titanium .....	Ti 48.1
Krypton .....	Kr 83.92	Tungsten .....	W 184.0
Lanthanum .....	La 139.0	Uranium .....	U 238.5
Lead .....	Pb 207.10	Vanadium* .....	V 51.0
Lithium .....	Li 6.94	Xenon .....	Xe 130.2
Lutecium .....	Lu 174.0	Ytterbium (Neoytterbium) Yb	172.0
Magnesium .....	Mg 24.32	Yttrium .....	Yt 89.0
Manganese .....	Mn 54.93	Zinc .....	Zn 65.37
Mercury* .....	Hg 200.6	Zirconium .....	Zr 90.6

## Organic Chemistry.

**New Method for Esterification of Alcohols by Halogen Acids.** GEORGES DARZENS (*Compt. rend.*, 1911, 152, 1314—1317).—

A general method for replacing the hydroxyl group by a halogen consists in treating the substance with thionyl chloride or bromide (2 mols.) in presence of a tertiary base (1 mol.). There is but little development of heat, and the reaction is complete in half an hour. Sulphur dioxide may be removed by heating at 80—110°, but this is not always necessary. The process gives yields exceeding 95%, and is stated to be free from the disadvantages associated with the use of a halogen hydride or the employment of phosphorus pentachloride. Dimethyl- and diethyl-aniline are the most suitable bases to use. As examples of its application, the conversion of *iso*amyl alcohol, dichlorohydrin, benzyl carbinol, and cinnamyl carbinol into the corresponding chloro-derivatives is mentioned. The method cannot be applied to phenols. *cyclo*Hexanol is converted into *cyclo*hexene through removal of hydrogen chloride from the unstable chloro-compound.

W. O. W. e

**Boiling Point of Mixtures of Water and [Ethyl] Alcohol.** C. MARILLER (*Bull. Assoc. chim. Sucr. Dist.*, 1911, 28, 768—770).—

The boiling point of mixtures of ethyl alcohol and water, containing 8 to 100% of alcohol, can be represented by means of the formula  $t = 78.4 + \sqrt{0.22 \frac{a \cdot e}{a}}$ , in which  $e$  and  $a$  denote respectively the percentages of water and alcohol in the mixture boiling at  $t^\circ$  under atmospheric pressure.

H. M. D.

**Synthesis of Tertiary  $\alpha$ -Keto-alcohols.** D. GAUTHIER (*Compt. rend.*, 1911, 152, 1259—1261. Compare this vol., i, 415).—An

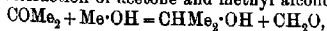
extension of the reaction previously described to the cyanohydrins of ketones.  $\beta$ -Methylbutanone- $\beta$ -ol,  $\text{OH} \cdot \text{CMe}_2 \cdot \text{COMe}$ , prepared by the action of magnesium methyl iodide on acetone cyanohydrin (cyano-*iso*-propyl alcohol), has b. p. 79°/730 mm., and forms a *semicarbazone*, m. p. 180°. This substance is not identical with the compound to which Schmidt and Austin (Abstr., 1903, i, 2) have ascribed the above constitution.

$\beta$ -Methylpentan- $\gamma$ -one- $\beta$ -ol,  $\text{OH} \cdot \text{CMe}_2 \cdot \text{COEt}$ , has b. p. 96—98°/725 mm.  $\gamma$ -Methylpentanone- $\gamma$ -ol,  $\text{OH} \cdot \text{CMeEt} \cdot \text{COMe}$ , has b. p. 94°/729 mm.

W. O. W.

**Chemical Action of Light.** XIX. GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1911, 44, 1280—1289. Compare Abstr., 1910, i, 299).—A mixture of acetone (1 part) and methyl alcohol (2 parts),

after being exposed to the action of light for over one year, was found to contain *isopropyl* alcohol, formaldehyde, ethylene glycol, and *iso*-butylene glycol,  $\text{OH} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{OH}$ . The two substances first-named are formed by the interaction of acetone and methyl alcohol:



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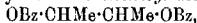
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whilst the formation of ethylene glycol and isobutylene glycol is due to a condensation of methyl alcohol with formaldehyde and acetone respectively.

Similar results have been obtained by replacing the methyl alcohol by ethyl alcohol. A mixture of acetone and ethyl alcohol, after exposure to light for nine months, gave the following products: (1) diacetyl, which was identified by means of its oxime, m. p. 344° (Fittig, Abstr., 1889, 490, gives 234.5°); (2) isopropyl alcohol; (3) *β*-methylbutylene *β*-glycol,  $\text{OH} \cdot \text{CMe}_2 \cdot \text{CHMe} \cdot \text{OH}$ ; (4) an oil, containing, amongst other substances, trimethylethylene glycol and butylene-*β*-glycol,  $\text{OH} \cdot \text{CHMe} \cdot \text{CHMe} \cdot \text{OH}$ . In order to separate the latter compound, advantage was taken of the fact that it undergoes the pinacol rearrangement when heated with dilute sulphuric acid at 130° less readily than methylbutylene glycol, which is converted under the same conditions into methyl isopropyl ketone. The distillate, after this treatment, was found to contain, besides methyl isopropyl ketone, a liquid, b. p. 149°, having the composition  $\text{C}_4\text{H}_{10}\text{O}_2$ . This substance is probably formed from methylbutylene glycol and butylene glycol by the loss of water:  $\text{C}_3\text{H}_8\text{O}_2 + \text{C}_2\text{H}_6\text{O}_2 = 2\text{H}_2\text{O} + \text{C}_4\text{H}_{10}\text{O}_2$ , but whether it is contained in the original mixture or is subsequently produced by the action of sulphuric acid has not been decided.

The *β*-butylene glycol, isolated from the mixture, gave, on treatment with phenylcarbimide, two isomeric *phenylurethanes*, the less soluble one having m. p. 175°, the other, m. p. 201–202°. These have the composition  $\text{NHPh} \cdot \text{CO} \cdot \text{O} \cdot \text{CHMe} \cdot \text{CHMe} \cdot \text{O} \cdot \text{CO} \cdot \text{NHPh}$ , and are considered by the authors to be the phenylurethanes of racemic and inactive butylene *β*-glycol. Two *dibenzoyl* derivatives,



were also obtained: a solid, crystalline form, m. p. 77° (monoclinic:  $a : b : c = 0.4170 : 1 : 0.3337$ ;  $\beta = 69.6^\circ$ ), and a liquid modification, b. p. 217–218°/16 mm.

With isopropyl alcohol and acetone the reaction is much simpler; the only product formed by exposing a mixture of these substances, in equal parts, to the action of light for nine months consists of pinacone.

With the object of discovering if a condensation of alcohol with aromatic ketones takes place under the influence of light, similar to that found in the case of acetone, the behaviour of benzophenone in ethyl-alcoholic solution has been re-investigated (compare Abstr., 1901, i, 329), but no evidence of such a condensation has been obtained.

F. B.

**Basic Properties of the Oxygen of Ethers.** DEMETRIUS K. TSAKALOTOS (*Bull. Soc. chim.*, 1911, [iv], 9, 519–523).—Determinations of the viscosities and densities of mixtures of (1) ethyl ether and acetic acid, and (2) ethyl ether and trichloroacetic acid, indicate that the first two substances do not form additive compounds with each other, whilst the second two form at least one (compare Tsakalotos and Guye, Abstr., 1910, ii, 826). The conclusion is drawn that ethereal oxygen is weakly basic and can only unite with strong acids.

T. A. H.

**Catalytic Decomposition of Formic Acid.** PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1911, 152, 1212—1215).—Substances which bring about catalytic decomposition of formic acid may be divided into three classes: (1) Those capable of effecting dehydrogenation; the products in this case contain only traces of formaldehyde. The following act in this way: palladium, platinum, rhodium, reduced copper, nickel and cadmium, zinc and stannous oxides; (2) catalysts effecting dehydration, namely, the oxides of titanium, tungsten, zirconium, aluminium, uranium and silicon; (3) substances acting in the same way as the foregoing, but in addition giving more or less formaldehyde, such as ferrous, manganous, chromic, magnesium, molybdenum, vanadium and glucinum oxides, lime, carbon and Jena glass. Since the nature of the products and their relative proportions depend on the catalyst employed, it is evident that these substances do not act merely by lowering the temperature at which the reactions become possible.

W. O. W.

**Direct Synthesis of Glycerides.** ITALO BELLUCCI and R. MANZETTI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 503—504).—In reply to Gianoli's claim for priority (Sixth Congress of Applied Chemistry, Rome, 1906; this vol., i, 349) to the authors (this vol., i, 259), the latter point out that Scheij (Abstr., 1899, i, 667) was the first to synthesise glycerides under reduced pressure.

T. H. P.

**The Systems: Fat-Alcohol.** ALBERT J. J. VANDEVELDE (*Bull. Soc. chim. Belg.*, 1911, 25, 210—216).—Butter-fat, coconut oil, and olive oil were separately brought into contact with different proportions of 94% alcohol at 37° until equilibrium was attained, and the composition of the fatty and alcoholic layers was then determined. Similar experiments were also made with a mixture of butter-fat and coconut oil.

H. M. D.

**Action of Ultra-violet Light on Lactic Acid.** MARC LANDAU (*Compt. rend.*, 1911, 152, 1308—1309. Compare Berthelot and Gaudechon, this vol., ii, 170; Euler, *ibid.*, ii, 452).—In addition to the liberation of gases when lactic acid is exposed to ultra-violet light, other changes occur involving the production of ethyl alcohol, pyruvic acid, and traces of an unidentified substance which reduces ammoniacal silver nitrate in the cold.

W. O. W.

**Oxidation of Higher Acetylenic Aliphatic Acids.** ALBERT ARNAUD and V. HASENFRATZ (*Compt. rend.*, 1911, 152, 1603—1606. Compare Abstr., 1902, i, 342—343).—In the oxidation of stearolic and tauric acids by nitric acid, the chain is broken between the two carbonyl groups of the diketonic acid which represents the first stage of oxidation. When potassium permanganate is employed, however, one carbonyl group is eliminated as carbon dioxide. This follows from the observation that on treatment with alkaline permanganate, stearolic acid gives nonoic and octoic acids (38%) with suberic and zelaic acids (53%), whilst tauric acid yields lauric and undecioic acids (55%) with glutaric and adipic acids (25%).

W. O. W.

**Studies on Tautomerism. IV. Desmotropy of Acetoacet Ester.** LUDWIG KNORR, O. RETHE, and H. AVERBECK (*Ber.*, 1914, 1138—1157).—The ketonic and enolic forms of ethyl acetoaceta have been isolated in a pure condition and their transformation studied. The ketonic ester is sparingly soluble in organic solvents at a low temperature, and therefore crystallises when its solutions are strongly cooled. It was isolated by cooling its solution in alcohol or a mixture of alcohol and ether to  $-78^{\circ}$ , and washing the crystals thus obtained with light petroleum or methyl ether until free from the enolic form, in a specially constructed apparatus, a sketch of which is given. All operations must be carried out in the complete absence of moisture. The ketonic ester crystallises in prisms or needles, which may be kept for a long time at a low temperature without undergoing any change. At the ordinary temperature it is slowly transformed into the equilibrium mixture, the change in the absence of catalytic influences being complete in the course of seven weeks. Small quantities may be distilled in the vacuum of the cathode light practically unchanged. It has b. p.  $40-41^{\circ}/2$  mm,  $n_D^{20}$  1.4225, and solidifies at  $-39^{\circ}$ , whereas the equilibrium mixture solidifies at  $-45^{\circ}$  to  $-43^{\circ}$ , and has b. p.  $39-40^{\circ}/2$  mm.,  $n_D^{20}$  1.423 to 1.4232. At the ordinary temperature, it gives the ferric chloride reaction like the equilibrium mixture, but this is ascribed to enolisation induced by the ferric chloride. At low temperatures the enolisation takes place less rapidly, and in these circumstances comparative tests show that the red coloration with ferric chloride is developed much more slowly in the case of the ketonic ester than with its equilibrium mixture.

The enolic ester is obtained by treating a suspension of ethyl sodioacetoacetate in light petroleum with gaseous hydrogen chloride in quantity just insufficient for complete decomposition, filtering free sodium chloride, and evaporating the filtrate as rapidly as possible under strongly diminished pressure, all operations being carried out at  $-78^{\circ}$  and in the complete absence of moisture. A sketch of the apparatus employed is given.

The enolic ester is a colourless oil, having an agreeable fruit odour; it has  $D_4^{20}$  1.0119,  $n_D^{20}$  1.4480, and solidifies in liquid air to glassy mass, which soon becomes crystalline. In a high vacuum and in small quantities, it distils at about  $33^{\circ}$  without undergoing appreciable change. Its enolic nature is shown by a much more rapid development of the ferric chloride reaction than is the case with the ketonic ester. In ethereal solution at  $-78^{\circ}$ , it gives at once an intense coloration with ethereal ferric chloride. Reasons are given in favour of the cis-configuration,  $\begin{array}{c} \text{H}-\text{C}-\text{CO}_2\text{Et} \\ | \\ \text{Me}-\text{C}-\text{OH} \end{array}$ , for the ester.

A large number of mixtures of the ketonic and enolic esters have been prepared, and their refractive indices determined; from the results thus obtained it is found that, at the equilibrium point, ethyl acetoacetate contains 2% of the enolic form (compare Hantzsch *Abstr.*, 1910, i, 811; K. H. Meyer, this vol., i, 350).

At low temperatures the enolic ester may be kept for a long time unchanged. At the ordinary temperature, it is transformed into the

course of ten to fourteen days into the equilibrium mixture, whilst at 90° the transformation is complete in one minute. The velocity of transformation has been determined refractometrically, and it is found to be enormously increased by the catalytic influence of both acids and bases. Contact with gaseous hydrogen chloride, soft alkali glass, and even exposure to air, transform the enolic ester into the equilibrium mixture in the course of a few seconds or minutes. In solution, the velocity of transformation at the ordinary temperature also increases, but diminishes rapidly with fall of temperature.

The influence of temperature on the equilibrium between the ketonic and enolic forms has been investigated by heating ethyl acetoacetate at various temperatures up to 181°, and then rapidly cooling, but no displacement of the equilibrium could be detected. Refractometric measurements showed that all specimens thus treated contained 2% of the enolic modification.

The equilibrium between the ketonic and enolic esters in the form of vapour varies, however, with the temperature and pressure. When ethyl acetoacetate is distilled under ordinary pressure and the vapour rapidly cooled, a distillate containing 10% of the enolic form was obtained, whilst by distilling slowly under diminished pressure and cooling the vapour rapidly to -78°, the proportion of enolic ester rises to 27—39%, and remains constant until the end of the distillation. According to the authors, the greater proportion of the enolic form in the distillate is due to its greater vapour pressure; it therefore distils over more rapidly, and since the equilibrium thus disturbed is quickly restored at the temperature of the distillation, the enolic ester is continuously replenished in the distillation flask. The distilled ester is far more rapidly transformed into the equilibrium mixture than the enolic ester, prepared from ethyl sodioacetoacetate. The view is expressed that this is due to the formation during the distillation of the trans-enolic ester, which has a greater velocity of transformation into the ketonic form than the cis-isomeride.

The relative proportions of the ketonic and enolic forms in equilibrium in various solvents have also been determined; the values obtained for the percentage of enolic ester vary from 2% in light petroleum to 31% in hexane.

By strongly cooling solutions of many other tautomeric substances, one of the forms crystallises out, whilst in other cases a separation may be effected by freezing and pressing out.

F. B.

**Action of Thionyl Chloride in Presence of a Tertiary Base on esters of Hydroxy-acids.** GEORGES DARZENS (*Compt. rend.*, 1911, 12, 1601—1603. Compare this vol., i, 513).—The method previously described for replacing the hydroxyl group by a halogen has been successfully applied to the esters of hydroxy-acids. Ethyl lactate gave a practically theoretical yield of ethyl  $\alpha$ -chloropropionate; pyridine is the best base to employ in this case. Ethyl succinate has been transformed into ethyl  $d$ -chlorosuccinate; less racemisation takes place than when phosphorus pentachloride is employed, and the product has  $[\alpha]_D^{20} + 31.20^\circ$ , whereas Walden found  $27.30^\circ$ .

In some cases dehydration occurs; thus ethyl *cyclohexan-1-ol-1-carboxylate* gives ethyl *cyclohexenecarboxylate*, whilst esters of the type  $\text{OH}\cdot\text{CRMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  are converted into the corresponding acrylates.

W. O. W.

**$\psi$ -Acid Esters in the Mesoxalic Ester Synthesis.** RICHARD S. CURTISS and JOHN A. KOSTALEK (*J. Amer. Chem. Soc.*, 1911, 33, 962—974).—It has been shown by Curtiss (*Abstr.*, 1906, i, 480) that when the gases evolved by the action of nitric acid on arsenious oxide are allowed to react with ethyl malonate at  $-10^\circ$ , ethyl mesoxalate is produced, together with an oily acid substance which was at first supposed to be ethyl isonitrosomalonate, but has now been found to consist of a mixture of acid esters containing nitrogen. From this mixture, ethyl nitromalonate and ethyl dinitroacetate have been separated by means of their potassium salts. The acid esters are colourless oils, whilst their potassium salts are coloured. Ethyl nitromalonate and its salts have been studied by Hantzsch (*Abstr.*, 1907, i, 556), who explains the variation in colour on the basis of differences in structure.

Ethyl dinitroacetate yields potassium salts of two forms, one yellow, which has been described by Bouveault and Wahl (*Abstr.*, 1903, i, 225), and the other red, the latter being known only in solution. The cold aqueous solution of the yellow form is also yellow, but becomes red when heated, and reverts to its original colour on cooling. The yellow form is dimorphous, crystallising in slender, monoclinic prisms or lustrous plates; it decomposes at  $194-195^\circ$ . On reduction with tin and hydrochloric acid, it yields ethyl glyoxylate and ammonia. When the potassium salt is heated with methyl or ethyl iodide and 50% alcohol in a sealed tube at  $100-110^\circ$ , a yellow, viscous, unstable oil is produced. The salt reacts more readily with ethyl sulphate, and yields potassium sulphate and nitrite and a mixture of oily products. On boiling potassium ethyl dinitroacetate (1 mol.) with alcoholic potassium hydroxide (2 mols.), a brilliant yellow salt is formed, which is probably a form of dipotassium *acido*-dinitroacetate; it decomposes violently at  $210^\circ$ . The ammonium and silver salts of ethyl dinitroacetate are described; the sodium, hydrazine, and aniline salts were also prepared.

Potassium ethyl nitromalonate, m. p.  $154^\circ$ , crystallises in dark yellow needles or hexagonal prisms. Hantzsch (*loc. cit.*) obtained a colourless form of this salt by the action of potassium carbonate on the colourless form of the ammonium salt. The ammonium salt, m. p.  $151^\circ$ , obtained by the action of dry ammonia on ethyl nitromalonate at  $-10^\circ$ , forms pale yellow, prismatic crystals. The white modification dissolves in alcohol or water to form a yellow solution.

If dry ammonia is passed into an ethereal solution of the crude product of the action of nitrogen oxides on ethyl malonate, the salts of ethyl nitromalonate and ethyl dinitroacetate are precipitated. When an excess of ammonia is added, an unstable red oil separates. The filtrate from the ammonium salts yields a crystalline substance, m. p.  $50^\circ$ , which forms flat, colourless needles.

E. G.

**New Complex Iridium Derivatives: Iridotetrachloro-oxalates and Iridotetrachlorides.** ALEXIS DUFFOUR (*Compt. rend.*, 1911, 152, 1393—1396).—The iridotetrachloro-oxalates are intermediate between the iridichlorides and the iridodichloro-oxalates previously described (Abstr., 1909, i, 762). The *sodium* salt,  $\text{Na}_3\text{IrCl}_4(\text{C}_2\text{O}_4)_2$ , was obtained in solution by heating sodium oxalate with aqueous sodium iridichloride. The *potassium* salt obtained from this by double decomposition crystallises with  $1\text{H}_2\text{O}$  in dark reddish-brown, orthorhombic prisms showing strong dichroism and double refraction. An aqueous solution gives no reaction for chloride or oxalate, but with silver nitrate yields an insoluble *silver* salt. The *rubidium*, *caesium*, and *ammonium* salts crystallise with  $1\text{H}_2\text{O}$ , and appear to be isomorphous with the potassium salt.

*Iridotetrachloro-oxalic acid*, prepared from the silver salt, is crystalline, but very unstable. In solution it decomposes into oxalic acid and a new acid,  $\text{HIrCl}_4$ , which has not been isolated. The existence of a substance of this constitution is assumed from the fact that the corresponding *barium* salt gives no silver chloride when treated with silver nitrate, but forms a green precipitate of the *silver* salt.

W. O. W.

**New Types of Irido-oxalic Acids and Irido-oxalates.** ALEXIS DUFFOUR (*Compt. rend.*, 1911, 152, 1591—1594. Compare preceding abstract).—Gialdini's irido-oxalic acid (Abstr., 1907, i, 1005) is best prepared by the action of hydrochloric acid on the silver salt. When freshly prepared, its aqueous solution is golden-yellow, but on exposure to air becomes brown, and, finally, emerald-green. The solution now contains a new acid arising from the elimination of a molecule of oxalic acid from the original substance. The corresponding *potassium* salt,  $\text{KIr}(\text{C}_2\text{O}_4)_2 \cdot 5\text{H}_2\text{O}$ , obtained by adding potassium hydroxide (1 mol.), occurs in highly refractive, dichroic, green crystals, which lose  $3\text{H}_2\text{O}$  at  $110^\circ$  without changing colour. On further treatment with potassium hydroxide (1 mol.), it forms an orange-red salt,  $\text{K}_2[\text{Ir}(\text{C}_2\text{O}_4)_2(\text{OH})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ . The corresponding *acid*,  $\text{H}_2[\text{Ir}(\text{C}_2\text{O}_4)_2(\text{OH})(\text{H}_2\text{O})] \cdot 5\text{H}_2\text{O}$ ,

forms monoclinic crystals, losing  $3\text{H}_2\text{O}$  over sulphuric acid and  $5\text{H}_2\text{O}$  at  $110^\circ$ ; on treatment with potassium hydroxide (1 mol.), yellow dichroic prisms of the salt,  $\text{KH}[\text{Ir}(\text{C}_2\text{O}_4)_2(\text{OH})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ , are obtained isomeric with the first-mentioned green salt, from which it can also be prepared by the action of heat on the aqueous solution.

W. O. W.

**Action of the Oxides of Lead on Potassium Tartrate.** FRANCIS C. KRAUSKOFF (*J. Amer. Chem. Soc.*, 1911, 33, 943—947).—The solubility of litharge in solutions of alkali tartrates (Kahlenberg and Hillyer, Abstr., 1894, i, 275; Kahlenberg, Abstr., 1896, ii, 6) and the supposed insolubility of red lead and lead dioxide in such solutions indicated a method for freeing red lead and lead dioxide from litharge and for estimating the amount of litharge in samples of these oxides. It has been found, however, that both red lead and lead dioxide are soluble to some extent in alkali tartrate solutions.

A study of the action of red lead and lead dioxide on potassium tartrate solutions has shown that these oxides dissolve without causing the evolution of oxygen. In the case of lead dioxide, the tartrate is oxidised and lead carbonate is precipitated, but red lead dissolves without appreciable oxidation of the tartrate. The rotatory power of potassium tartrate solution is diminished by the addition of either litharge or red lead. Red lead causes a slightly greater diminution of the rotation than an equivalent quantity of litharge, and it is therefore evident that red lead is not reduced to litharge before dissolving.

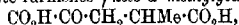
E. G.

**Dibasic Ketonic Acids.** EDMOND E. BLAISE and HENRI GAGLI (*Bull. Soc. chim.*, 1911, [iv], 9, 451—458, 458—464).—A more detailed account is given of the general method for the preparation of dibasic ketonic acids described already (Abstr., 1908, i, 713; 1909, i, 134, 362; 1910, i, 487, 542), and syntheses of new acids of this type are described. Ethyl oxalysuccinate, b. p. 170—175°/12—13 mm., is a pale yellow oil which must be distilled rapidly in order to avoid much decomposition. Wislicenus and Nassauer's ester was probably chiefly ethyl ethanetricarboxylate (Abstr., 1895, i, 506). On condensation with propyl iodide, ethyl oxalysuccinate gives ethyl

O-propyloxalysuccinate, 
$$\text{OPr}^a \text{---} \text{C} \text{---} \text{C} \text{---} \text{CO}_2\text{Et}$$
 b. p. 195—198°

15 mm. or 190—191°/13 mm. (Abstr., 1908, i, 713). On hydrolysis by hydrobromic or hydrochloric acid, this yields as one product (*loc. cit.*)  $\alpha$ -ketoglutaric acid,  $\text{CO}_2\text{H} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , which gives a yellowish-green coloration with ferric chloride and furnishes a *phenylhydrazone*, m. p. 260° (approx. decomp.), separating from dilute alcohol in small, yellow crystals; and a *semicarbazone*, m. p. 220° (approx.), crystallising from warm water. Its reaction with hydrazine hydrate has been described by Gabriel (Abstr., 1909, i, 259). *Ethyl  $\alpha$ -ketoglutarate*, b. p. 144°/13 mm., obtained by esterification of the acid in a closed tube at 120°, is a colourless liquid; the *semicarbazone*, m. p. 114°, is crystalline. Attempts to prepare the acid anhydride were unsuccessful.

Ethyl  $\alpha$ -oxalyl  $\beta$ -methylsuccinate (Abstr., 1908, i, 713) furnishes a crystalline *p*-nitrophenylhydrazone. On heating, the ester furnishes *propane  $\alpha$ - $\beta$ -tricarboxylic acid*, m. p. 170° (decomp.), which on further heating yields methylsuccinic acid. On hydrolysis by acids, ethyl methylloxalysuccinate furnishes  $\gamma$ -keto- $\alpha$ -methylglutaric acid,



as a viscous liquid which is not volatile without decomposition. It yields an unstable *oxime*, m. p. 162° (approx.), a *semicarbazone*, m. p. 141—142°, a *phenylhydrazone*, m. p. 171—172°, and *p*-nitrophenylhydrazone, m. p. 163°, all of which are crystalline. The acid cannot be regenerated from the semicarbazone; the phenylhydrazone on dehydration, by heating at 140°, furnishes 1-phenyl-5-methylpyridazin-6-one-3-carboxylic acid, m. p. 134°, crystallising from water in lamellae. By the direct action of hydrazine hydrate on methyl ketoglutaric acid, 5-methylpyridazin-6-one-3-carboxylic acid, m. p. 175°, is obtained.

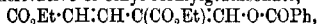
*Ethyl ketomethylglutarate*, b. p. 144—145°/15 mm., obtained by

esterifying the acid in the usual way, is a colourless liquid; it forms a crystalline *additive product* with sodium hydrogen sulphite, and yields a *semicarbazone*, m. p.  $98^{\circ}$ , and a *p-nitrophenylhydrazone*, m. p.  $109-110^{\circ}$ , both of which are crystalline. T. A. H.

**Ethyl Formylglutaconate and its Isomerides.** WILHELM WISLICENUS and MARGARITA VON WRANGELL (*Annalen*, 1911, 381, 367-384. Compare Wislicenus and Bindemann, *Abstr.*, 1901, i, 361).—The oily product formed by leaving ethyl formylglutaconate dissolved in moist ether for two to three days is shown to be a polymeride, namely,  $C_{20}H_{28}O_{10}$ , of the original ester. It is characterised by its oily consistency and by the red coloration it gives with ferric chloride. Moisture is essential for its formation; in dry benzene solution the original ester is stable, and can be kept for months; with the dry solid in a desiccator at the ordinary temperature the transformation is extremely slow, but rise of temperature favours the change. Small amounts of acid, on the other hand, retard the transformation. With sodium ethoxide the polymeride yields an orange-yellow salt, but is not so reactive as the original ester, for example, it does not react with bromine, hydrogen bromide, phenylhydrazine, or benzoyl chloride. Its *copper* derivative forms a deep green, slimy mass, which was obtained as a solid, m. p.  $97^{\circ}$ , on one occasion only. The structure suggested for the oily polymeric form is

$CO_2Et \cdot CH_2 \cdot CH \cdot C(CO_2Et) \cdot CH(OH) \cdot CH(CO_2Et) \cdot CH \cdot C(CO_2Et) \cdot CHO$ , and this formula is in agreement with the fact that when heated at  $120^{\circ}$  under slight pressure the oil yields ethyl trimesate, formic acid, and ethyl acetate, and also with the formation of an additive compound,  $C_{27}H_{33}O_{11}N$ , with phenylcarbimide. It is probably that the original ester is first transformed into the tautomeric aldo-form before polymerisation occurs.

The *benzoyl* derivative of ethyl formylglutaconate,



crystallises from ether in colourless needles, m. p.  $63.5^{\circ}$ , and the corresponding *p-nitrobenzoyl* derivative,  $C_{17}H_{11}O_6N$ , in colourless needles, m. p.  $117^{\circ}$ .

The *phenylcarbimide* additive product,  $C_{17}H_{19}O_6N$ , forms colourless plates, m. p.  $74^{\circ}$ . When bromine is added to its chloroform solution, the ester yields a *dibromide*,  $C_{16}H_{13}O_6Br_2$ , as an oil which does not react with ferric chloride. When distilled under 14 mm. pressure, it loses hydrogen bromide and yields an oily *ethyl bromoformylglutaconate*,  $CO_2Et \cdot C(CH_2OH) \cdot CH \cdot CBr \cdot CO_2Et$ , which gives an intense red coloration with ferric chloride. Potassium ethoxide transforms the oily bromo-ester into an *isomeric* solid, which crystallises from ether in colourless needles, m. p.  $55-56^{\circ}$ , and gives a violet coloration with ferric chloride. The *copper* derivative,  $(C_{16}H_{13}O_6Br)_2Cu$ , crystallises from benzene in small prisms, m. p.  $144-145^{\circ}$ .

*Ethyl bromocoumalate*,  $CO_2Et \cdot \begin{matrix} CH & O \\ \diagdown & \diagup \\ CH & CBr \end{matrix} \cdot CO$ , obtained by distilling ethyl bromoformylglutaconate, crystallises from alcohol in colourless prisms, m. p.  $94-95^{\circ}$ , and on hydrolysis with the theoretical



amount of potassium hydroxide solution yields Feist's furan-2:4-dicarboxylic acid (Abstr., 1901, i, 557).

Ethyl formylglutaconate dichloride forms a colourless oil, and when distilled under reduced pressure yields ethyl dichlorodihydrocoumalate,  $\text{CO}_2\text{Et}\cdot\text{C}\begin{array}{c} \text{CH} \\ \text{CHCl}\cdot\text{CHCl} \end{array}\text{O}\text{CO}$ , as an oil with b. p. 175–180°/18–20 mm.

J. J. S.

Tetrolaldehyde ( $\Delta^2$ -Butinal). PAUL L. VIGUIER (*Compt. rend.*, 1911, 152, 1490–1493. Compare Abstr., 1909, i, 691).—Diethoxybutinene is best prepared by the action of ethyl orthoformate on magnesium allylene bromide. When the acetal is hydrolysed with 10% aqueous oxalic acid, *tetrolaldehyde*,  $\text{CMe}_2\text{C}\cdot\text{CHO}$ , is produced, and may be isolated by distillation in steam and extraction with ether. This substance is a colourless, mobile liquid with an intensely irritating odour, m. p.  $-26^\circ$ , b. p. 27–28°/34 mm., 106.5–107° under ordinary pressure,  $D_0^{20}$  0.944,  $D_{17}^{20}$  0.9265,  $n_D^{20}$  1.4467. It shows the usual reactions of an aldehyde and forms a very soluble compound with sodium hydrogen sulphite. The *semicarbazone* has m. p. 158°. The *oxime* crystallises in long needles, subliming at about 100°, m. p. 108–109°; at the ordinary temperature it changes slowly into methylisooxazolone (compare Claisen, this vol., i, 491).

Tetrolaldehyde reacts with hydrazine hydrate to give a *hydrazone*, b. p. 63–65°/15 mm.,  $D_{16}^{15}$  0.9768,  $n_D^{15}$  1.530; the corresponding *azine* forms yellow needles, m. p. 123–124°. The hydrazone unites with phenylthiocarbimide, producing a *phenylthiosemicarbazone*, m. p. 114–116° (decomp.). 5-Methylpyrazole is formed when the aldehyde is heated with potassium hydroxide.

W. O. W.

The Pinacolin Transformation. I. J. LINDNER (*Monatsh.*, 1911, 32, 403–426).—The researches of previous investigators leave little doubt that pinacones and pinacolins have respectively the constitutions, for example,  $\text{OH}\cdot\text{CMe}_2\cdot\text{CMe}_2\cdot\text{OH}$  and  $\text{CMe}_2\cdot\text{COMe}$ . During the conversion of the former into the latter by dilute acids, therefore, a methyl group has shifted from the one tertiary carbon atom to the other. The author hopes to show that the change is explicable by Erlenmeyer's theory of the intermediate production of a cyclopropane derivative, despite Montagne's criticism (Abstr., 1905, i, 445, 524). A suggestion is advanced to counter Montagne's objection that in the conversion to 4:4':4''-tetraclorobenzopinacone into the corresponding pinacolin, the halogen atoms are still in the para-position, whereas by Erlenmeyer's theory they should be in the ortho- or meta-positions, to the tertiary carbon atom. A serious objection to Erlenmeyer's theory, however, is Lieben's statement (Abstr., 1905, i, 167) that the pinacolin transformation is possible only with (purely aliphatic) pinacones which contain the group  $\text{CMe}\cdot\text{OH}$ . Attention is drawn to the mobility of aromatic groups in glycols; thus Thörner and Zincke have shown that acetophenonepinacone yields only the pinacolin,  $\text{CMePh}_2\cdot\text{COMe}$  (compare also Tiffeneau, Abstr., 1907, i, 130). This mobility, which may be due to the unsaturated character of the aromatic nucleus and its consequent ability to enter into ring formation, is in

favour of Erlenmeyer's theory. The theory would be proved by the isolation of the intermediately formed *cyclopropanol* derivative, for example,  $\text{OH} \cdot \text{CMe}_2 \begin{smallmatrix} \diagup \text{CMe}_2 \\ \diagdown \text{CH}_2 \end{smallmatrix}$ .

With this end in view the author has prepared the two methyl ethers of acetonepinacone. An intimate mixture of the pinacone (1 mol.) and sodium is carefully warmed, and the resulting sodium derivative is heated for several days with methyl iodide. The separation of the two ethers is very difficult. The *methyl ether*,  $\text{OMe} \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{OH}$ , has b. p. 148—149°; the *dimethyl ether* has b. p. 144°; both are colourless liquids, with a pleasant odour recalling that of the pinacone.

A preliminary experiment with boric anhydride having shown that acetonepinacone can be thereby transformed into the pinacolin, the two ethers have been separately heated at 140° with this oxide, but in both cases the pinacolin, not the desired *cyclopropanol* derivative, is formed. The methyl ether is recovered unchanged after being heated with sodium acetate at 120—140°, or with barium oxide at 200°, but is partly converted into the pinacolin after being shaken with 25% sulphuric acid and kept for two weeks. The *acetate*,  $\text{OMe} \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{OAc}$ , b. p. 179—180°, of the methyl ether, obtained by the action of acetic anhydride and 3 drops of concentrated sulphuric acid for twelve days, has also been heated with boric anhydride at 110°, but methyl acetate and pinacolin are the only products which have been identified.

Dimethylisopropylcarbinol, which is most conveniently prepared from methyl isopropyl ketone and magnesium methyl iodide, has also been examined in the hope that it might yield a *cyclopropane* derivative,  $\text{CMe}_2 \begin{smallmatrix} \diagup \text{CHMe} \\ \diagdown \text{CH}_3 \end{smallmatrix}$ , under the influence of acids. However, 20% sulphuric acid at 130° converts it almost quantitatively into  $\beta$ -dimethyl  $\Delta^3$ -butylene, whilst the action of boric anhydride, which is different, has not yet been fully examined. The preceding experiments, although not fulfilling the author's hopes, indicate that the formation of esters plays an important part in the pinacolin transformation, which is a specific action of acids. C. S.

**Ethyl Derivatives of Acetone.** ERNST ZERNER (*Compt. rend.*, 1911, 152, 1599—1601).—Using Haller and Bauer's method (*Abstr.*, 1910, i, 219—300), the author has prepared the tri-, tetra-, penta-, and hexa-ethyl derivatives of acetone.

$\gamma\gamma$ -Triethylheptan- $\delta$ -one,  $\text{CET}_3 \cdot \text{CO} \cdot \text{CHET}_3$ , has b. p. 237.5—238.5°/761 mm.  $\gamma\gamma\epsilon\epsilon$ -Tetraethylheptan- $\delta$ -one,  $\text{CET}_3 \cdot \text{CO} \cdot \text{CET}_3$ , m. p. 44°, b. p. 274—275°/759 mm., has an apple-like odour, and does not undergo the usual scission when treated with sodamide. W. O. W.

**Action of Hydrogen Peroxide on  $\alpha$ -Diketones.** JACOB BÖRSEKEN, (Mile.) LICHTENBELT, MILO, and VAN MARLEN (*Rec. trav. chim.*, 1911, 80, 142—147).—The normal course of the oxidation of  $\alpha$ -ketonic acids, such as pyruvic, phenylglyoxylic, *p*-chlorophenylglyoxylic, and thienyl-

glyoxylic acids, by hydrogen peroxide results in the elimination of the ketonic group. The presence of a methyl group near the ketonic group, however, induces by-reactions; thus trimethylpyruvic acid is partly converted into isobutyric acid, and 2:4:6-trimethylphenylglyoxylic acid into phthalic acid.

Diacetyl is oxidised by hydrogen peroxide, yielding acetic acid, but not carbon dioxide; oxalic acid is only slowly and partly oxidised, yielding carbon dioxide, whilst oxamide, oxanilide, and oxanilic acid are almost unattacked, showing that the hydroxyl group largely, and the amino-group almost entirely, prevents the oxidation of the  $\alpha$ -diketones.

$\beta$ -Naphthaquinone is oxidised by hydrogen peroxide, yielding an unsaturated dibasic acid, m. p. 173—175° (o-carboxycinnamic acid?), whilst stearoxylic acid is quantitatively converted into azelaic and pelargonic acids; the latter oxidation furnishes another proof of the constitution of oleic acid.

C. S.

**The Destruction of Dextrose by Light.** ADOLF JOLLES (*Biochem. Zeitsch.*, 1911, 33, 252. Compare Mayer, this vol., i, 423).—The author reiterates his statement, that in alkaline solutions of dextrose when kept, the polarisation sinks to zero. The reaction must be carried out in well-closed flasks.

S. B. S.

**Action of Ultra-violet Light on Sucrose.** HENRI BIERRY, VICTOR HENRI, and ALBERT RANC (*Compt. rend.*, 1911, 152, 1629—1632. Compare Abstr., 1910, i, 625; this vol., i, 255).—The first action on sucrose of the light from a quartz-mercury lamp is to hydrolyse the sugar, and then to effect profound decomposition of the two hexoses, leading ultimately to the formation of formaldehyde and carbon monoxide.

W. O. W.

**Inversion of Sucrose in Ultra-violet Radiation.** HANS FOX EULER and H. OHLSEN (*J. Chim. Phys.*, 1911, 9, 416—422).—Aqueous solutions of sucrose were exposed in a quartz cell to the radiation from a quartz-mercury lamp. The solutions became heated to about 79° in twenty minutes, and were maintained at that temperature. The rate of hydrolysis appeared to be independent of the quantity of sugar present, and did not follow the unimolecular law. An acidic substance was progressively formed in the solutions, and the inversion was not greater than could be attributed to the action of this acid.

R. J. C.

**Action of Alkalis on Chloraloses.** MAURICE HANRIOT and ANDRÉ KLING (*Compt. rend.*, 1911, 152, 1398—1399. Compare Abstr., 1910, i, 95).—Chloralose suffers decomposition when treated with aqueous alkalis, but if heated in sealed tubes with ammonia and methyl alcohol, it forms a dichloro-derivative,  $C_7H_{11}O_6 \cdot CHCl_2$ , needles, m. p. 156—157°; the tribenzoyl derivative of this substance crystallises in needles, m. p. 192°. On hydrolysis, it yields dichloroacetaldehyde and dextrose, whilst nitric acid oxidises it to an amide,  $C_7H_9O_6Cl_2 \cdot CO \cdot NH_2$ , m. p. 161—162°. The corresponding acid is

obtained in needles, m. p. 129—130°, by treating this with nitrous acid; it very readily forms a *lactone*, from which well defined salts are prepared by the action of alkalis. W. O. W.

**Action of Ammonia on Chloraloses.** MAURICE HANRIOT and ANDRÉ KLING (*Compt. rend.*, 1911, 152, 1596—1599. Compare preceding abstract).—The reaction previously described is general for chloraloses. Ammonia withdraws an atom of chlorine from  $\alpha$ -chloralose, replacing it by hydrogen, forming a compound,  $C_6H_{12}O_6Cl_2$ , long needles, m. p. 165°, in aqueous solution  $[\alpha]_D + 9.96^\circ$ ; the *dibenzoyl* derivative has m. p. 146°. When the substance is treated with nitric acid, it forms a vitreous, feebly acidic *lactone*.

Galactochloralose and ammonia yield a compound isomeric with the foregoing, but existing in two modifications; one separates from water in crystals, m. p. 96°, but is changed in the second modification, m. p. 133°, on crystallisation from chloroform. The *dibenzoyl* derivative has m. p. 116°. Nitric acid oxidises the compound to mucic acid, whilst hydrochloric acid converts it into dichloroacetaldehyde and probably galactose.

The compound,  $C_7H_{10}O_6Cl_2$ , obtained from arabinochloralose has m. p. 88—89°,  $[\alpha]_D - 19.72^\circ$ ; the *dibenzoyl* derivative has m. p. 90.5°. Nitric acid converts it into an acid,  $C_8H_8O_6Cl_2$ , m. p. 215°, and possibly this is accompanied by trihydroxyglutaric acid.

W. O. W.

**An Experiment to Demonstrate the Reducing Properties of Cellulose.** ROLAND SCHOLL (*Ber.*, 1911, 44, 1312—1314. Compare Scholl and Berblinger, *Abstr.*, 1904, i, 110; Scholl, *ibid.*, 1907, i, 540).—A simple experiment which demonstrates the reducing properties of cellulose in a few minutes is as follows: The specimen to be tested is digested for a few seconds with a dilute solution obtained by boiling flavanthren with water, dilute sodium hydroxide solution, and solid sodium hyposulphite. After washing, the yellow dye is developed by exposing the fabric to the air for a few minutes, or by treatment with hypochlorite solution. By heating the yellow fabric to boiling with a 2*N*-sodium hydroxide solution, the blue colour is restored. The length of time required for the reduction depends upon the amount of hydrocelluloses and oxycelluloses present in the original specimen. Oxycelluloses give an immediate blue colour, but when the oxycelluloses are removed by previous boiling with dilute sodium hydroxide solution, a longer time is required for the development of the blue colour, and the alkaline extract produces the coloration more rapidly than does pure alkali. Other vat dyes, such as pyranthrone or anthraquinoneazine, can be used in place of flavanthren. In the ordinary process of printing without specific reducing agents, the reduction is brought about by the dextrin, gum, etc., used. J. J. S.

**Partial Hydrolysis of Tunicate Cellulose. Formation of Cellobiose.** EMIL ABDERHALDEN and GÉZA ZEMPLÉN (*Zeitsch. physiol. Chem.*, 1911, 72, 58—62).—The mere obtaining of dextrose from tunicin, the cellulose of tunicate animals, does not establish its identity

with vegetable cellulose. Further proofs of the identity or close relationship are now adduced, namely: (1) by the action of acetic anhydride in the presence of sulphuric acid, an acetyl compound (octa-acetylcellobiose) was obtained with the same melting point, solubility, composition, and optical activity as the product similarly obtained from filter paper; (2) the osazones of the cellobioses are also identical; (3) by saponification of the acetyl compound by means of barium hydroxide in the cold, crystallised cellobiose was obtained.

W. D. H.

**Phosphates of Uranyl and of Amines.** LÉONCE BARTHE (*Compt. rend.*, 1911, 152, 1396—1397).—Double phosphates of the type  $B^+H_2UO_4PO_4$  have been prepared by saturating an aqueous solution of phosphoric acid with an amine, and adding a solution of uranyl acetate drop by drop. The compounds are precipitated in a pale yellow colloidal condition, and when dried in a vacuum become horny. They are very stable, and are not decomposed at  $100^\circ$ .

*Methylamine uranyl phosphate*,  $NH_2Me \cdot UO_4PO_4$ , has been obtained in this way, and also the corresponding *ethylamine* and *trimethylamine* salts.

W. O. W.

**Preparation of Tetramethylenediamine [ $\alpha\delta$ -Diaminobutane]** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 232073).—A method for the technical preparation of  $\alpha\delta$ -diaminobutane has not previously been known; it is now found that a satisfactory yield can be obtained by treating adipodiamide,  $NH_2 \cdot CO \cdot [CH_2]_4 \cdot CO \cdot NH_2$ , with a halogen in aqueous alkaline solution; the amide dissolves, and the temperature rises to  $70^\circ$ ; the reaction is completed by heating on the water-bath.

F. M. G. M.

**Syntheses of Polypeptides. Derivatives of  $\alpha$ -Aminobutyric Acid and their Behaviour towards Peptolytic Ferments.** EMIL ABDERHALDEN, HSING LANG CHANG, and ERICH WURM (*Zeitsch. physiol. Chem.*, 1911, 72, 24—36).—*dl*- $\alpha$ -Formylaminobutyric acid,  $CH_3Me \cdot CH(CO_2H) \cdot NH \cdot CHO$ , obtained by the action of formic acid on  $\alpha$ -aminobutyric acid, crystallises from water in colourless plates, m. p.  $153^\circ$ , and can be resolved into its optically active components by means of brucine. The brucine salt, which is less soluble, is that of formyl-*l*-aminobutyric acid, although the formyl acid is dextrorotatory. On crystallisation the m. p. of the acid falls, probably owing to the removal of the formyl group.

When *dl*- $\alpha$ -aminobutyric acid is fermented with yeast in the presence of sucrose, the *d*-acid is destroyed before the *l*-acid, so that the product isolated by Fischer's esterification method is levorotatory.

The action of active yeast extract on the three dipeptides, glycyl-*d*-aminobutyric acid and the corresponding *l*- and *dl*-compounds, has been investigated. The *l*-compound is not affected, but both the *d*- and *dl*-compounds are attacked.

From these results the conclusion is drawn that the  $\alpha$ -aminobutyric acid which occurs in nature is the *d*-acid, as almost invariably it is the naturally-occurring acid which is more readily attacked by ferments.

*Chloroacetyl-dl*- $\alpha$ -aminobutyric acid,  $CH_2Cl \cdot CO \cdot NH \cdot CHMe \cdot CO_2H$ ,

crystallises from ethyl acetate and light petroleum in pointed plates, m. p.  $130^{\circ}$  (corr.), and  $[\alpha]_D^{20} - 18.14^{\circ}$ . The corresponding *d*-compound has m. p.  $119^{\circ}$  (corr.) after sintering at  $112^{\circ}$ . *Glycyl-dl- $\alpha$ -aminobutyric acid*,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CHEt}\cdot\text{CO}_2\text{H}$ , crystallises from dilute alcohol in pointed needles, m. p.  $231^{\circ}$  (corr.), and the corresponding *d*-acid forms long needles, m. p.  $223^{\circ}$  (corr.), and has  $[\alpha]_D^{20} - 12.24^{\circ}$ .

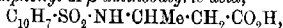
*Glycyl-l- $\alpha$ -aminobutyric acid* has m. p.  $222^{\circ}$  (corr.) and  $[\alpha]_D^{20} + 18.29^{\circ}$ . *L*-Alanine is best prepared from *d*-alanine from silk. The *d*-alanine is transformed into *l*- $\alpha$ -bromopropionic acid, and this on treatment with 10% aqueous ammonia at the ordinary temperature yields an alanine with  $[\alpha]_D^{20} - 10.3^{\circ}$  (in form of the hydrochloride). J. J. S.

The Walden Inversion. VI.  $\beta$ -Aminobutyric Acid. EMIL FISCHER and HELMUTH SCHEIBLER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1911 566—586. Compare Abstr., 1910, i, 622).— $\beta$ -Aminobutyric acid has been resolved into the optically active components by the crystallisation of the camphorsulphonate of its methyl ester. The active amino-acid may be converted into hydroxy-acid by means of nitrous acid or by treatment with nitrosyl chloride and subsequent boiling of the chlorobutyric acid formed with water. The two methods result in the formation of optically opposed hydroxy-acids, although the reactions are not so simple as with the  $\alpha$ -amino-acids. In at least one of them a Walden inversion takes place, and this phenomenon is therefore extended to the  $\beta$ -series.

*d*-Aminobutyric acid is prepared in quantity by heating crotonic acid with ammonia in an autoclave for twenty-four hours at  $130$ — $140^{\circ}$ . The methyl ester, prepared by esterification with methyl alcohol and hydrogen chloride and decomposition of the hydrochloride so formed with ammonia, is a colourless, odorous liquid, b. p.  $54$ — $55^{\circ}/13$  mm.,  $D_4^{20}$  0.993.

*d*- $\beta$ -Aminobutyric acid has m. p.  $191$ — $192^{\circ}$  (corr.). The copper salt is best prepared by repeated evaporation with copper acetate.

$\beta$ -Naphthalenesulphonyl-*dl*- $\beta$ -aminobutyric acid,



crystallises in prisms, which sinter at  $163^{\circ}$ , m. p.  $166$ — $167^{\circ}$  (corr.). Methyl-*d*- $\beta$ -iminobutyrate has b. p.  $135^{\circ}/12$  mm.,  $144$ — $145^{\circ}/17$  mm.,  $D_4^{20}$  1.044.

*l*- $\beta$ -Aminobutyric acid crystallises in well-formed, thick prisms, decomp. about  $220^{\circ}$ ,  $[\alpha]_D^{20} - 35.2^{\circ}$  ( $\pm 0.2^{\circ}$ ); the *d*-isomeride is very similar,  $[\alpha]_D^{20} + 35.3^{\circ}$  ( $\pm 0.2^{\circ}$ ); in *N*-hydrochloric acid it has  $[\alpha]_D^{20} + 29.7^{\circ}$ ; in *N*-sodium hydroxide,  $[\alpha]_D^{20} + 14.7^{\circ}$ .

By the action of nitrous acid on *l*- $\beta$ -aminobutyric acid, *d*- $\beta$ -hydroxybutyric acid is obtained, the product being about 62% racemised. Nitrous acid acts in the same way optically on the methyl ester, methyl-*d*- $\beta$ -hydroxybutyrate being formed.

By the action of nitrosyl chloride on *d*- $\beta$ -aminobutyric acid, *l*- $\beta$ -chlorobutyric acid is obtained, but little racemisation taking place.

*d*- $\beta$ -Chlorobutyric acid crystallises in large prisms, m. p.  $43$ — $44.5^{\circ}$ ,  $[\alpha]_D^{20} + 49.8^{\circ}$  ( $\pm 0.2^{\circ}$ ). E. F. A.

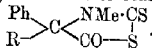
**Methylated Polypeptides.** EMIL ABDERHALDEN and KARL KAUTZSCH (*Zeitsch. physiol. Chem.*, 1911, **72**, 44—49).—*Trimethyl-leucylglycine*,  $\text{CHMe}_3 \cdot \text{CH}_2 \cdot \text{CH}(\text{NMe}_3 \cdot \text{OH}) \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$  or  $\text{CHMe}_3 \cdot \text{CH}_2 \cdot \text{CH} \begin{smallmatrix} \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \\ \text{NMe}_3 \longrightarrow \text{O} \end{smallmatrix} \text{CO}$ , may be obtained by methylating *dl*-leucylglycine with methyl iodide in the presence of methyl alcohol and *N*-potassium hydroxide at the ordinary temperature, and is best isolated as the *platinichloride*,  $(\text{C}_{11}\text{H}_{23}\text{O}_3\text{N}_3)_2\text{PtCl}_6$ , which crystallises from water in brilliant orange-red prisms or plates. The *aureichloride*,  $\text{C}_{11}\text{H}_{23}\text{O}_3\text{N}_3\text{AuCl}_4$ , also crystallises from water in orange-yellow prisms, m. p. 170—172°, after softening at a lower temperature. The *picrate* crystallises from dilute alcohol in brilliant lemon-yellow prisms, m. p. 228—229° (corr.), and decomposing at 240—250°. J. J. S.

**Salts and Esters of Alkylaminodithiocarbamic Acids.** ERNEST FOURNEAU (*Bull. Soc. chim.*, 1911, [iv], **9**, 532—536).—Methylaminoacetic acid reacts in ether with carbon disulphide to form the corresponding *dithiocarbamate*,

$\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{NMe} \cdot \text{CS} \cdot \text{S} \cdot \text{NH}_2 \cdot \text{Me} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , m. p. 77°, which crystallises in colourless, inodorous, hexagonal tablets, and is very soluble in alcohol or water. On adding mercuric chloride to the aqueous solution, the *mercury* derivative,

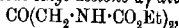
$(\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{NMe} \cdot \text{CS}_2)_2\text{Hg}$ , m. p. 148°, is formed. It crystallises from boiling alcohol in slender, yellow needles, and is soluble in acetone. The corresponding *mercury* derivative of the *propyl* ester,  $(\text{CO}_2\text{Pr} \cdot \text{CH}_2 \cdot \text{NMe} \cdot \text{CS}_2)_2\text{Hg}$ , m. p. 86°, resembles its lower homologue. On adding sodium hydroxide to an alcoholic solution of either of these substances, the unstable compound,  $(\text{CO}_2\text{Na} \cdot \text{CH}_2 \cdot \text{NMe} \cdot \text{CS}_2)_2\text{Hg}$ , is precipitated in the form of small, colourless needles.

Similar series of derivatives are formed from the ethyl esters of ethylaminoacetic and methylaminohydroxyisobutyric acids, whilst ethyl phenylmethylaminoacetate reacts with carbon disulphide to form the *dithiazolone*,



T. A. H.

**Derivatives of *s*-Diaminoacetone.** ANTOINE P. N. FRANCHIMONT and J. V. DUBSKY (*Rec. trav. chim.*, 1911, **30**, 177—182).—The reaction of *s*-diaminoacetone hydrochloride with ethyl chloroformate under the conditions employed by Franchimont and Friedmann (*Abstr.* 1907, i, 832) yields *ethyl acetone- $\alpha$ -diurethane*,

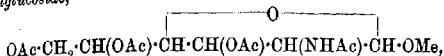


m. p. 136—137°. This substance is not attacked by boiling acetic anhydride alone, but in the presence of a little zinc chloride yields the *diacetyl* derivative,  $\text{CO}(\text{CH}_2 \cdot \text{NAc} \cdot \text{CO}_2\text{Et})_2$ , m. p. 61—62°. It nitrates readily, forming the  *$\alpha$ -dinitro*-compound,  $\text{C}_9\text{H}_{14}\text{O}_6\text{N}_4$ , m. p. 56—57°.

*Tetra-acetyl-1:3-diaminoacetone*,  $\text{CO}(\text{CH}_2 \cdot \text{NAc})_2$ , obtained by boiling 1:3-diacetylaminoacetone (*loc. cit.*) for three hours with a large excess of acetic anhydride, forms large needles, which soften at 98°, and have m. p. 108°. C. S.

**A Tetra-acetyl Aminoglucoside.** MARSTON L. HAMLIN (*J. Amer. Chem. Soc.*, 1911, 33, 766—769).—The work described in this paper has been forestalled by the publication of Irvine, McNicoll, and Hynd's paper on new derivatives of *d*-glucosamine (*Trans.*, 1911, 89, 350). These authors' results are confirmed, but it is found that bromotriacetylglucosamine hydrobromide does not melt, but darkens at 138—148°, and chars at 153° (uncorr.).

When a solution of bromotriacetylglucosamine hydrobromide in methyl alcohol is shaken with silver carbonate and filtered, the filtrate boiled with acetic anhydride, the methyl alcohol and acetic anhydride removed by distillation in a vacuum, and the residue boiled with a further quantity of acetic anhydride, *tetra-acetylglucosamine methylglucoside*,



m. p. 150.5° (uncorr.), is obtained, which forms a white, crystalline powder. This compound is not a derivative of the aminoglucoside prepared by Fischer and Zach (this vol., i, 117), since the latter on hydrolysis yields the hydrochloride of an amino-sugar which is not identical with glucosamine hydrochloride. E. G.

**Preparation of Acetamide.** MARTIN A. ROSANOFF, LOUISE GULICK, and HERBERT K. LARKIN (*J. Amer. Chem. Soc.*, 1911, 33, 974—977).—Acetamide can be prepared in good yield by the following method.

Dry ammonium acetate is prepared by neutralising glacial acetic acid with powdered ammonium carbonate at about 50°, allowing the product to cool, draining the crystals, and pressing them between filter paper. A mixture of this ammonium acetate (1 mol.) and glacial acetic acid (1.5 mols.) is boiled for five hours under a reflux condenser. The product is rapidly distilled, and the distillate is submitted to slow fractional distillation, using a two-bulb Wurtz dephlegmator. Three fractions are collected: (1) below 180°; (2) between 180° and 213°, and (3) above 213°. The second fraction is redistilled, and the portion passing over above 213° is added to fraction 1. The portion with high-boiling point, after it has solidified, is pressed between filter paper, and the dry crystals thus obtained consist of almost pure acetamide (b. p. 214—216°). The yield from 100 grams of ammonium acetate amounts to over 60 grams, or about twenty grams more than can be obtained by the Hoffmann-Gattermann method. The yield cannot be increased by carrying out the reaction in sealed tubes. E. G.

**Acetylation of Substituted Acetamides.** ANTOINE P. N. FRANCHIMONT and J. V. DUBSKY (*Rec. trav. chim.*, 1911, 30, 183—185).

The formation of tetra-acetyldiaminoacetone (this vol., i, 528) is merely an instance of a general reaction, whereby mono- and disubstituted amines are acetylated by boiling with a large excess of acetic anhydride. Thus acetmethylamide is converted into diacetylethylamine, acetethylamide into diacetylethylamine, and *s*-diacetylethylenediamine into *tetra-acetylethylenediamine*,  $\text{NAc}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NAc}_2$ , m. p. 156—157°. C. S.



**Ammonium Cyanate and Carbamide.** RICHARD ESCALAS (*Chem. Zeit.*, 1911, 35, 595).—The author (with H. KÖPKE) has found that when carbamide is sublimed in a vacuum at 160–190°, the sublimate consists of ammonium cyanate. He remarks that if Wöhler had endeavoured to purify his synthetical urea by sublimation, his famous discovery might never have been made.  
L. DE K.

**Catalytic Action of Ferric Thiocyanate.** H. COLIN and A. SÉNÉCHAL (*Compt. rend.*, 1911, 152, 1586–1587).—The authors consider that ferric thiocyanate is not strictly speaking a specific peroxydase. Its action in bringing about oxidation of phenols in presence of hydrogen peroxide is partly due to decomposition of the salt, whereby peroxy-acids of sulphur are formed. Potassium thiocyanate acts in the same way as the iron salt, but not to such a marked extent.  
W. O. W.

**Aliphatic Nitro-compounds. X. Hydroxamyl Chlorides.** WILHELM STEINKOPF and BORIS JÜRGENS (*J. pr. Chem.*, 1911, [ii], 83, 453–470. Compare Abstr., 1910, i, 280).—The substance, previously recorded as  $\beta$ -oximino-oxalimino-chloride from its reactions and methods of formation, may be chloro-oximinoacetamide, produced, for example, from nitroacetonitrile and hydrogen chloride in dry ether, by the following series of reactions:  $\text{NO}_2\cdot\text{CH}_2\cdot\text{CN} \xrightarrow{\text{HCl}} \text{NOH}\cdot\text{C}(\text{OH})\cdot\text{CN} \rightarrow \text{NOH}\cdot\text{CCl}\cdot\text{CN} + \text{H}_2\text{O} \rightarrow \text{NOH}\cdot\text{CCl}\cdot\text{CO}\cdot\text{NH}_2$ . At first sight the explanation appears improbable, because it is unlikely that the water formed in the second reaction can convert the nitrile into the amide in the presence of the large excess of ether. However, the discovery that hydrogen chloride converts ethyl nitroacetate in dry ether into ethyl chloro-oximinoacetate shows that the first two phases of the series above can occur. The fact that the third phase does occur, and that the so-called  $\beta$ -oximino-oxalimino-chloride is really chloro-oximinoacetamide, is proved by the action of aqueous sodium carbonate on the substance in the cold, whereby an odour of a nitrile oxide is observed, and furoxandicarboxylamide (dinitroso peroxide of succinamide) is formed.

From analogy to the preceding, the so-called  $\alpha$ -oximino-oxalimino-chloride, m. p. 173–174° (decomp.), produced from methazonic acid and hydrogen chloride in ether (*loc. cit.*), must be chloro-oximino-acetaldoxime (chloroglyoxime),  $\text{NOH}\cdot\text{CCl}\cdot\text{CH}\cdot\text{NOH}$ . This is so, because not only is the substance converted by thionyl chloride in dry ether into chloro-oximinoacetonitrile,  $\text{CN}\cdot\text{CCl}\cdot\text{NOH}$  (which is too unstable to be analysed, but yields with aniline, *anilino-oximinoacetonitrile*,  $\text{NHPh}\cdot\text{C}(\text{CN})\cdot\text{NOH}$ , m. p. 138–139°), but also the identity of the substance with Hantzsch's chloroantiglyoxime, m. p. 161° (Abstr., 1892, 693) (the m. p. can be raised to 168° by repeated crystallisation), is proved by the fact that the two substances form the same acetyl derivative, m. p. 163–164°, and diacetyl derivative, m. p. 90–5°. Moreover, a moist ethereal solution of the chloro-oximinoacetonitrile is hydrolysed by hydrogen chloride, yielding chloro-oximinoacetamide. *Chloro-oximinoacetic acid*,  $\text{NOH}\cdot\text{CCl}\cdot\text{CO}_2\text{H}$ , decomp. 129°, is obtained by keeping for three weeks a suspension of potassium

nitroacetate in dry ether saturated with hydrogen chloride in the cold.

In Nägeli's chloroamphiglyoxime (Abstr., 1883, 728) the chlorine atom and one of the hydroxyl groups have the *anti*-configuration, because the substance is insensitive to alkalis and does not yield a nitrile oxide with sodium carbonate. Now an aqueous solution of this antichloroamphiglyoxime reacts with aniline to form a salt,  $\text{NOH}\cdot\text{CCl}\cdot\text{CH}\cdot\text{NOH}\cdot\text{NH}_2\text{Ph}$ , m. p.  $114^\circ$  (decomp.). This behaviour not only illustrates the stability of the halogen atom in antihydroxamyl chlorides, but may also serve for the characterisation of such substances, because other hydroxamyl chlorides, in which the chlorine atom and the hydroxyl group have the *syn*-configuration, react with aniline to form anilino-derivatives by substitution of the halogen atom. The authors deduce from the preceding that the *a*- and the  $\beta$ -oximinohydroxamic acids previously described (*loc. cit.*) have the *anti*- and the *syn*-configurations respectively.

By chlorinating a cold solution of chloroantiglyoxime in dilute hydrochloric acid, antichloroglyoxime ( $\beta$ -dichloro- $\beta$ -dioximinoethane),  $\text{NOH}\cdot\text{CCl}\cdot\text{CCl}\cdot\text{NOH}$ , m. p.  $201^\circ$ , is obtained, which yields the odour of a nitrile oxide by heating or by treatment with sodium carbonate, forms a dibenzoyl derivative, m. p.  $217^\circ$ , and reacts with aniline to form  $\beta$ -dianilino- $\beta$ -dioximinoethane.

Ethyl iodo-oximinooacetate,  $\text{CO}_2\text{Et}\cdot\text{Cl}\cdot\text{NOH}$ , m. p.  $95-96^\circ$ ; iodo-oximinooacetamide,  $\text{NOH}\cdot\text{Cl}\cdot\text{CO}\cdot\text{NH}_2$ , yellow crystals, decomp.  $154-155^\circ$ ; iodoantiglyoxime,  $\text{NOH}\cdot\text{Cl}\cdot\text{CH}\cdot\text{NOH}$ , m. p.  $136^\circ$ , and antidi-iodoglyoxime,  $\text{NOH}\cdot\text{Cl}\cdot\text{Cl}\cdot\text{NOH}$ , decomp.  $172^\circ$ , are obtained by heating the corresponding chloro-compounds with a solution of sodium iodide in acetone. antichloroamphiglyoxime does not react with sodium iodide in acetone, another instance of the stability of the chlorine atom in antichloro-oximinoo-compounds. C. S.

**Friedel and Crafts' Reaction.** JACOB BOESEKEN (*Rec. trav. chim.*, 1911, 30, 148-150).—The formation of *as*-heptachloropropane from tetrachloroethylene and chloroform in the presence of aluminium chloride (this vol., i, 173) is typical of the reactions between trichloroethylene and chloroform, trichloroethylene and carbon tetrachloride, dichloroethylene and chloroform, and dichloroethylene and carbon tetrachloride; in every case the initial reaction is the simple addition of the two molecules.

The preceding explains the nature of the Friedel and Crafts' reaction. Three molecules must be present: (a) an unsaturated molecule, (b) a molecule which can be so activated that it can combine with the unsaturated molecule, (c) a catalyst which activates the molecules in (a) and (b). The possibility of the reaction is determined by the loss of free energy. The initial action is due to the encounter of the two molecules with the catalyst; in the case of benzene and other unsaturated cyclic systems the initial additive product, a derivative of hydrogenbenzene, etc., cannot be isolated, because by elimination of hydrogen chloride or the like it is converted into a system containing less free energy. C. S.

**Friedel and Crafts' Reaction. XI. Action of Sulphur Monochloride on Benzene, Chlorobenzene, and Toluene.** JACOB BÖESEKEN and D. A. WITTOR KONING (*Rec. trav. chim.*, 1911, 30, 116—136).—The reaction between benzene and sulphur monochloride in the presence of aluminium chloride is more complex than that previously recorded (*Abstr.*, 1905, i, 583), since diphenyl disulphide is always formed. The formation of the disulphide, if produced by a primary reaction, indicates that sulphur monochloride may have a symmetrical constitution.

The authors have examined quantitatively the action of sulphur monochloride on an excess of benzene, chlorobenzene, or toluene in the presence of an excess of aluminium chloride. When the reaction is completed, the sulphur monochloride has been entirely destroyed. Estimations are made of the sulphur present in the free state or combined as hydrogen sulphide, aromatic sulphide, aromatic disulphide, thianthren, or in the side-chain (in the case of toluene).

The reaction is simplest in the case of chlorobenzene; hydrogen sulphide and a thianthren are not formed, the products consisting of sulphur, di-*p*-chlorophenyl sulphide, and di-*p*-chlorophenyl disulphide (identified by oxidising it to chloronitrobenzenesulphonic acid by nitric acid, D 1.5). The reaction with benzene yields sulphur, hydrogen sulphide, diphenyl sulphide, diphenyl disulphide, thianthren, and a trace of phenyl mercaptan.

The reaction is still more complicated in the case of toluene; in addition to substances corresponding with the preceding, a small amount of dibenzyl sulphide (and disulphide?) is formed by substitution in the side-chain.

Despite these quantitative examinations, a clear picture of the reaction of sulphur monochloride and benzene (or chlorobenzene or toluene) cannot be drawn, because the primary reaction is obscured by secondary reactions due to the action, in the presence of the catalyst, of the liberated sulphur on the benzene and the diphenyl sulphide, and to the decomposition of the disulphide.

C. S.

**The System Propylbenzene-Antimony Trichloride.** BOUS N. MENSCHUTKIN (*J. Chim. Phys.*, 1911, 9, 314—322).—Propylbenzene, b. p. 157°/765 mm., becomes viscous on cooling, and solidifies below -100° to an isotropic mass, which has no definite melting point. When small proportions of antimony chloride are present, crystals of an additive compound separate on cooling. The compound usually has the formula  $\text{SbCl}_3 \cdot \text{C}_6\text{H}_5\text{Pr}$ , m. p. +1.5°, but sometimes consists of  $2\text{SbCl}_3 \cdot \text{C}_6\text{H}_5\text{Pr}$ , m. p. +9° to +10°, which is less soluble.

There are two distinct liquidus curves, representing the stable and labile compounds respectively. These curves cut the antimony trichloride liquidus at +1° and +8.5°, representing two distinct eutectics. The two liquidus curves are practically parallel, the difference being 8° near the eutectic points, and about 11° at 9% antimony trichloride concentration. The less fusible compound was not obtained spontaneously above 15% of antimony chloride, but could be easily obtained by sowing the more concentrated solutions.

According to the phase rule, the more soluble, more fusible com-

pound should be labile, whereas in the experiments the more fusible compound was the more readily obtainable.

R. J. C.

**Bromination of Some Hydroaromatic Compounds.** FERNAND BODROUX and FELIX TABOURY (*Compt. rend.*, 1911, 152, 1252—1254; *Bull. Soc. chim.*, 1911, [iv], 9, 595—601).—*cyclo*Hexane is converted into an oily monobromo-derivative when treated with bromine in sunlight; further treatment with bromine changes this into 1:2-dibromocyclohexane. The bromination of *cyclo*hexane, menthene, and thymomenthene in presence of aluminium bromide leads to the production of viscous liquids. Dibromocyclohexane and *cyclo*hexene under the same conditions give hexabromobenzene. Methylcyclohexane and  $\Delta^2$  and  $\Delta^4$ -methylcyclohexenes yield pentabromotoluene amongst other products. 1:3-Dimethylcyclohexane furnishes a mixture of isomeric tetrabromoxylenes.

W. O. W.

**Action of Sulphur on Aromatic Sulphones.** JACOB BÖESEKEN (*Rec. trav. chim.*, 1911, 30, 137—141).—When heated with rather more than 1 atom of sulphur at 250—275° in a current of dry carbon dioxide, the following sulphones do not yield sulphides, as does diphenylsulphone (Krafft and Vorster, *Abstr.*, 1894, i, 88), but decompose in a characteristic manner. 4:4'-Dichlorodiphenylsulphone yields *p*-dichlorobenzene and sulphur dioxide; 4:4'-dibromodiphenylsulphone decomposes similarly, but less readily. 4-Chloro-4'-bromodiphenylsulphone yields *p*-chlorobromobenzene. 4-Bromophenyl-*p*-tolylsulphone yields hydrogen sulphide, water, hydrogen bromide, and a little red oil.

C. S.

**Action of Dichloromethane on Di-*p*-tolylmethane.** JAMES LAYAUX (*Compt. rend.*, 1911, 152, 1400—1402. Compare *Abstr.*, 1905, i, 43, 125, 640, 698; 1906, i, 25; 1907, i, 150, 256).—To solve the problem of the constitution of the supposed 1:6- and 2:7-dimethylantracenes previously obtained by the action of dichloromethane and aluminium chloride on a mixture of isomeric ditolylmethanes, the condensation has been repeated on a pure specimen of di-*p*-tolylmethane. The latter prepared by the action of trioxymethylene on toluene in presence of sulphuric acid, occurs in needles, *n*. *p*. 28° (Ador and Rillet give 22—23°; Weiler, below -15°). It was found, however, that the pure hydrocarbon gave the same mixture of dimethylantracenes, indicating that aluminium chloride has brought about a transposition similar to that which it effects in converting *n*-propyl into isopropyl derivatives.

W. O. W.

**Hydrogenation by means of (1) Spongy Palladium and Sodium Hypophosphite, (2) Nickel and Sodium Hypophosphite.** PIERRE BRETEAU (*Bull. Soc. chim.*, 1911, [iv], 9, 515—517, 518—519. Compare this vol., i, 123).—Spongy palladium, precipitated from a solution of the chloride by sodium hypophosphite, decomposes water in presence of sodium hypophosphite, forming hydrogen and sodium hydrogen phosphite, and this mixture is useful as a reducing agent. In boiling alcohol, it reduces phenanthrene to the tetrahydride, and nitro- or dinitro-derivatives to the corresponding amines.

In the second paper it is shown that nickel in powder form, prepared by adding sodium hypophosphite to a hot solution of nickel sulphate, also decomposes water in presence of sodium hypophosphite. This mixture does not reduce phenanthrene, although it converts nitro-derivatives into the corresponding amines.

T. A. H.

**Compounds which Cause the Red Coloration of Aniline. II. Effect of Sunlight in the Absence of Oxygen and Oxidising Influences and a Comparison with the Behaviour of Mono- and Di-methylaniline.** HARRY D. GIBBS (*Philippine J. Sci.*, 1910, 5, 419—435. Compare Abstr., 1910, i, 550).—Aniline purified by various processes is sealed in glass tubes either in a vacuum or in an atmosphere of hydrogen, and exposed to sunlight for many (51—60) days during the summer months. The liquid acquires a very deep red, almost black, colour. The products are azophenine, benzene, and ammonia. The rate of coloration appears to increase with the pressure of the hydrogen in the tube. Aniline in tubes containing carbon dioxide colours very much less rapidly, the rate of coloration being greatest when the pressure of the gas is least. Methylaniline in an atmosphere of hydrogen also becomes red in sunlight (methylaniline is present among the products), whilst dimethylaniline is only slightly coloured, the coloration probably being due to impurities.

From these and the previous experiments on aniline (*loc. cit.*) and phenol (Abstr., 1909, i, 221, 640), it seems that the fixation of the labile hydrogen atom destroys the sensibility of the molecule to chemical change produced by sunlight. Attention is called to the fact that the introduction of methyl or ethyl groups into certain dyes to produce methyl or ethyl ethers, increases the fastness of the dye to light.

C. S.

**Mechanism of the Elimination of Halogens by Aromatic Amines.** IWAN OSTROMISLENSKY and PAWEŁ ALABKIEFF (*J. pr. Chem.*, 1911, [ii], 83, 506—512).—Hitherto an explanation has not been attempted of the fact that certain aromatic amines (aniline, phenylhydrazine, quinoline, pyridine) eliminate the halogen from various olefine dihalogenides with the regeneration of the original olefine. Thus the authors show that when stilbene dibromide is heated with dry pyridine for twelve hours on the water-bath, about 87% of the halogen is eliminated as hydrogen bromide, stilbene itself being formed. Consequently, in such reactions the hydrogen of the halogen acid must have been withdrawn from the aromatic amine, and, furthermore, must have been withdrawn from the aromatic nucleus, since the elimination in question can be effected by tertiary amines. It follows, therefore, that unstable groups, such as  $\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , must be formed. From these groups, by intramolecular change, polymerisation, etc., probably are formed the resinous substances which are almost invariably produced in the reactions in question. The formation of benzidine itself has never been observed in such reactions.

The authors' explanation accounts for the formation of tetramethyldiaminodiphenylethane observed by Schoop when dimethylaniline and ethylene dibromide are heated for eight days in the water-bath.

C. S.

**Catalytic Hydrogenation of Cyclic Oximes. Synthesis of Arylamines.** ALPHONSE MAILHE and MARCEL MURAT (*Bull. Soc. chim.*, 1911, [iv], 9, 464—468).—The reduction of aliphatic oximes to amines by means of finely divided metals has been described already (Abstr., 1905, i, 571, 635), and this work has now been extended to cyclic oximes. These are reduced less easily than the aliphatic oximes. The normal reaction is the formation of a mixture of the corresponding primary and secondary amines, the latter predominating, but in addition other reactions occur. The water formed leads to the regeneration of the parent ketone, and a part of the primary amine formed is decomposed, forming ammonia and olefinic hydrocarbons, the latter being in part reduced to the saturated hydrocarbons by the action of the metal; thus aminophenylbutane furnishes with hot, finely-divided nickel, ammonia, phenylbutylene, and phenylbutane. Except in the case of benzophenoneoxime this decomposition of the primary amine formed occurs to a large extent in all the cases tried.

The following new compounds were obtained: Acetophenoneoxime gave the *secondary amine*,  $\text{NH}(\text{CHMePh})_2$ , b. p. 295—298° (approx.),  $D^{20}_D$  1.018,  $n_D$  1.573. Propiophenoneoxime gave the *secondary amine*,  $\text{NH}(\text{CHEtPh})_2$ , b. p. 310—315°, the *hydrochloride* of which has m. p. 206° (approx. decomp.). Butyrophenoneoxime, m. p. 49°, b. p. 248°, furnished the *primary amine*,  $\text{CHPrPh}\cdot\text{NH}_2$ , b. p. 240°,  $D^{20}_D$  0.9813,  $n_D$  1.534, and a small quantity of *secondary amine*, b. p. 320° (approx.). Benzophenoneoxime gave a 70% yield of benzhydramine with some *dibenzhydramine*, m. p. 126°, the *hydrochloride* of which melts at 300° (approx. decomp.).

*o*-Methylcyclohexanoneoxime furnished the *primary amine*, b. p. 150°, and the *secondary amine*, b. p. 260° (approx. decomp.), the *hydrochloride* of which has m. p. 225° (approx. decomp.). The isomeric *meta*-*secondary amine* has b. p. 265° (decomp.), whilst the *para*-*secondary amine* has b. p. 265° (approx. decomp.).

Menthoneoxime yields *dimenthylamine*, b. p. 305°, the *hydrochloride* of which has m. p. 207° (approx. decomp.).

T. A. H.

**Quantitative Examination of the Introduction of One Atom of a Halogen into Phenol.** ARNOLD F. HOLLEMAN and I. J. RINKES (*Rec. trav. chim.*, 1911, 30, 48—100).—The authors have plotted the freezing-point curve of mixtures of *o*- and *p*-bromophenol, using specially purified materials; the eutectic point is at  $-11.7^\circ$ .

By brominating phenol with exactly the calculated amount (1 mol.) of bromine, either as vapour diluted with air or carbon dioxide or in a solvent, it is possible to conduct the operation quantitatively in such a way that no phenol remains unattacked and no dibrominated products are formed. After the bromination is complete and the solvent, if such has been used, has been removed by suitable methods (which are described), the product is distilled as completely as possible in a vacuum and the freezing point of the distillate is determined; reference to the freezing-point curve then gives the composition of the mixture, providing it consist only of *o*- and *p*-bromophenols. That the *meta*-isomeride is never produced is proved in the following way. The

brominated product is nitrated by nitric acid, D 1.52, at  $-5^{\circ}$ , the resulting nitrated bromophenols are treated with methyl-alcoholic sodium methoxide (1 mol.), the alcoholic solution is added to water acidified with nitric acid after twenty minutes, the phenolic substances are removed by ether, and the aqueous solution is tested with silver nitrate; the absence of a precipitate of silver bromide proves that no halogen has been eliminated from the nitrated bromophenols by the sodium methoxide, and therefore that no *m*-bromophenol was originally present, since this is the only bromophenol which yields by nitration a product containing nitro-groups in the ortho- and para-positions to the bromine atom. A distinct turbidity of silver bromide was produced when a mixture of *o*- and *p*-bromophenols containing 1% of the meta-isomeride was examined by the preceding process.

The presence of only *o*- and *p*-bromophenols in the product of the bromination of phenol is also proved by adding to the product (the composition of which has been ascertained from its freezing point) the amount of *o*-bromophenol required to bring its composition to that of the eutectic mixture; the freezing point is then found to be that, or very nearly that, of the eutectic mixture,  $-11.7^{\circ}$ .

The percentages of *p*-bromophenol obtained are as follows: 97.4% at  $-30^{\circ}$ , 92.8% at  $0^{\circ}$ , 86.2% at  $30^{\circ}$ , with carbon disulphide as solvent; 91.2% at  $15^{\circ}$ , 87.5% at  $30^{\circ}$ , 86.8% at  $60^{\circ}$ , with glacial acetic acid as solvent; 88.6% at  $30^{\circ}$ , with carbon tetrachloride as solvent; 90.2% at  $60^{\circ}$ , 90.7% at  $90^{\circ}$ , 81.6% at  $131^{\circ}$ , 79.4% at  $153^{\circ}$ , and 77% at  $180^{\circ}$ , without a solvent. The increase with the temperature in the percentage of *o*-bromophenol is much less than might be expected from references in the literature; also, for example at  $30^{\circ}$ , the composition of the mixture apparently is almost independent of the nature of the solvent.

*o*-Bromophenol has been prepared by brominating phenol without a solvent at  $170^{\circ}$  and fractionating the product; in addition to the usual form, m. p.  $5.5^{\circ}$ , a second modification of *o*-bromophenol has been discovered which solidifies at  $-10^{\circ}$  (compare Ostromisslensky, Abstr., 1907, i, 120).

The chlorination of phenol without a solvent has been performed at  $40^{\circ}$ ,  $90^{\circ}$ , and  $155^{\circ}$ , the percentages of *p*-chlorophenol, determined from the freezing-point curve of *o*- and *p*-chlorophenols, being 47.3, 50.2, and 48.8 respectively. It should be noted that the percentage of the para-isomeride is much less than that obtained by bromination, and remains nearly constant between  $40^{\circ}$  and  $155^{\circ}$ .

The quantitative conversion of phenol into iodophenols by direct iodination cannot be performed; even with a large excess of phenol the product contains unchanged substance and polyiodophenols. The main product, however, is *p*-iodophenol, the following method being very convenient for obtaining this substance. A solution of iodine in potassium iodide is added to an excess of aqueous phenol. Sodium hydroxide is added until the mixture is decolorised, and finally concentrated hydrochloric acid. The resulting oil is distilled at  $76^{\circ}$ /0.8 mm., whereby unchanged phenol is almost entirely removed. The residue is finally recrystallised from petroleum. C. S.

**Dyeing with Picric Acid.** GEORG VON GEORGIEVICS (*Monatsh.*, 1911, 32, 319—327).—The rule that the presence of sulphuric or other acid is essential for the adsorption of an acid dye by the fibre does not hold for picric acid at concentrations between about 0.008 and 0.017%, for the author finds that the amount of picric acid adsorbed from aqueous solutions of these concentrations is almost the same when an amount of sulphuric acid approximately equal to that of the picric acid is added to the bath.

Walker and Appleyard (*Trans.*, 1896, 69, 1334) have shown that the adsorption of picric acid by silk at 60° is such that the expression  $C^{2.64}/C'$  = constant, where  $C$  and  $C'$  are the concentrations of the dye in the fibre and in the bath respectively. The partition is independent of the temperature, the author's experiments at the ordinary temperature yielding the same result with the exception that the root exponent is 2.64 instead of 2.7. In the author's experiments the concentration of the picric acid varies from 0.02 to 0.4%. At the former concentration the value of the expression  $C^{2.64}/C'$  is very much below the mean value, a result which possibly may be due to the prolonged time requisite for equilibrium to be attained in very dilute solutions. The colour can be removed from the dyed silk by repeated treatment with acetone at the ordinary temperature.

The dyeing of animal fibres by acid dyes is often attributed to the formation of molecular compounds between the dye and the fibre. This explanation appears doubtful in the light of the following experiments. When the molecular compound naphthalene picrate is washed with water, the washings soon contain a constant amount, 0.08% of picric acid; naphthalene, introduced into a solution of 0.08% picric acid, does not form any picrate. Silk containing 3% of picric acid is washed with water, and the washings contain about 0.003% of picric acid. If the dyeing of the silk is due to the formation of a molecular compound analogous to naphthalene picrate, it is to be expected that silk will not adsorb any dye from a 0.003% solution of picric acid; experiment shows, however, that at this or even smaller concentrations the silk removes almost the whole of the picric acid from the solution.

Experiments are described which seem to indicate that the darkening of picric acid by exposure to the air is due to salt formation (ammonium picrate?). Also the fact that wool, dyed by picric acid in the cold, acquires a deeper tone by boiling with water (*Abstr.*, 1906, i, 420) may be due to the formation of picrates of the basic decomposition products of the wool. It is still unexplained, however, why aqueous solutions of picric acid darken by boiling, even in the presence of a little hydrochloric acid.

C. S.

**The Separation of *p*-Chloro-*m*-cresol** ( $\text{CH}_3 : \text{OH} : \text{Cl} = 1 : 3 : 6$ ) from Mixtures of *m*- and *p*-Cresol. FRITZ RASCHIG (*D.R.-P.* 232071).—The action of sulphuryl chloride (or chlorine) on a cooled solution of the technical mixture of *m*- and *p*-cresols is selective; if only sufficient chlorine is introduced to react with the *m*-cresol this alone is attacked, and on subsequent distillation (at atmospheric pressure)



the *p*-cresol will pass over at 200°, followed at 235° by pure *p*-chloro-*m*-cresol. A certain amount of *o*-chloro-*m*-cresol, b. p. 196°/760 mm., is also formed, and passes over with the *p*-cresol, from which it is subsequently separated; it is a colourless liquid with a camphor-like odour, and D<sub>4</sub><sup>15</sup> 1.215.

F. M. G. M.

**Magnesium Derivative of Fluorene.** VICTOR GRIGNARD and CHARLES COURTOT (*Compt. rend.*, 1911, 152, 1493—1495).—Fluorene forms a magnesium derivative when heated at 135° with magnesium ethyl bromide in xylene. In addition to fluorene-carboxylic acid, the following substances have been obtained from it by the usual methods.

*tert*-Fluorenylfluorenol, rose-coloured crystals, m. p. 195—196°; the corresponding ethyl ether,  $\text{C}_6\text{H}_4 > \text{C}(\text{OEt})\text{CH} < \text{C}_6\text{H}_4$ , crystallises in yellow needles, m. p. 174°; the chloride forms pale yellow crystals, m. p. 157—158°. Fluorenyldiphenylcarbinol was prepared in the same way as the corresponding indenyl derivative (this vol., i, 193).

*tert*-1-Indenylfluorenol forms a methyl ether, m. p. 115—116°, when its solution in methyl alcohol is treated with hydrogen chloride; under the same conditions diphenyl-1-indenylcarbinol undergoes dehydration. In general, the *tert*-fluorenols are more stable than the corresponding diphenylcarbinols.

W. O. W.

**Chlorides and Bromides of Diphenyl Sulphide.** KARL FRIEß and WILHELM VOGT (*Annalen*, 1911, 381, 337—346. Compare Böeseken, this vol., i, 41; Fromm and Raiziss, *Abstr.*, 1910, i, 554).—Diphenyl sulphide combines with chlorine when the dry gas is led into a benzene solution of the sulphide; the *dichloride*,  $\text{SPh}_2\text{Cl}_2$ , thus obtained forms pale yellow, flat prisms, which decompose when warmed, yielding mono- and di-chloro-substituted derivatives of diphenyl sulphide. In contact with atmospheric moisture, they yield hydrogen chloride and diphenylsulphoxide.

4:4'-Dichlorodiphenylsulphide *dichloride*,  $\text{SCl}_2(\text{C}_6\text{H}_4\text{Cl})_2$ , obtained from either diphenyl sulphide or its 4:4'-dichloro-derivative, forms compact, yellow, prismatic crystals, m. p. 95° (decomp.), and on treatment with water yields 4:4'-dichlorodiphenylsulphoxide,  $\text{SO}(\text{C}_6\text{H}_4\text{Cl})_2$ , which crystallises from light petroleum in compact prisms, m. p. 143°. The sulphoxide yields a pale violet-coloured solution in concentrated sulphuric acid, and is readily reduced to the sulphide by means of hydrobromic acid.

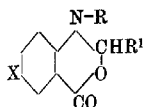
Diphenyl sulphide *dibromide*,  $\text{SPh}_2\text{Br}_2$ , obtained by the action of bromine on a well-cooled solution of diphenyl sulphide in hexane, forms orange-coloured needles, and even at the ordinary temperature passes over into substituted derivatives of diphenyl sulphide.

4:4'-Dibromodiphenyl sulphide *dibromide*,  $\text{C}_{12}\text{H}_8\text{Br}_4\text{S}$ , forms glistening, dark red plates, and yields a *perbromide*,  $\text{C}_{12}\text{H}_8\text{Br}_6\text{S}$ , in the form of brownish-red prisms.

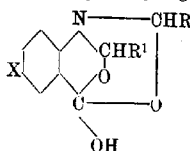
4:4'-Dibromodiphenylsulphoxide,  $\text{SO}(\text{C}_6\text{H}_4\text{Br})_2$ , separates from alcohol in compact, glistening, lance-shaped crystals, m. p. 152°, which dissolve readily in concentrated sulphuric acid, yielding a pale violet solution.

J. J. S.

**Preparation of Anthranilic Acid Esters Containing a Substituted Group in the para-Position to the Amino-group.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 231687).—When the aldehyde-condensation products of para-substituted anthranilic acids with the constitution I or II (where R and R<sub>1</sub> are hydrogen, alkyl,



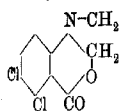
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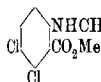
(II.)

aryl, or alkylaryl groups) are treated with esterifying agents, the aldehyde-groups are eliminated and the corresponding anthranilic ester obtained.

*Anhydromethylene-3:4-dichlorophenylglycine-2-carboxylic acid* (annexed formula), m. p. 246° (decomp.), separates in long needles when a warm methyl-alcoholic solution of 3:4-dichlorophenylglycine-2-carboxylic acid (264 parts) is treated with 30% formaldehyde solution (105 parts).



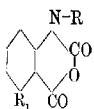
*Methyl 3:4-dichlorophenylglycine-2-carboxylate* (annexed formula), m. p. 76–78°, is prepared by heating the foregoing anhydro-base in methyl-alcoholic solution with concentrated sulphuric acid at 70° during twelve to fifteen hours, any acid ester which is simultaneously produced being removed subsequently by careful treatment with an alkali hydroxide.



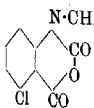
*Methyl tetrachloroanthranilate*, NH<sub>2</sub>·C<sub>6</sub>Cl<sub>4</sub>·CO<sub>2</sub>Me, needles, m. p. 120–121°, is obtained by heating tetrachloroanthranilic acid with a mixture of methyl alcohol, methylal, and sulphuric acid at 40–50° during twenty-four hours.

F. M. G. M.


**Preparation of Substituted Anthranilic Acid Esters.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 231962. Compare Abstr., 1889, i, 996; 1899, i, 939).—It is found that substituted anthranilic acid esters may be obtained in quantitative yield by treating the isatoic acids of the annexed general formula (where R is hydrogen, alkyl, aryl, or alkylaryl groups, and R<sub>1</sub> is a halogen) with esterifying agents.



*3-Chlorophenylglycine-2-carboxylic acid*, leaflets, m. p. 175° (prepared from 6-chloroanthranilic acid), when treated with carbonyl chloride in alkaline solution yields 6-chloroisatoacetic acid (annexed formula), a colourless, insoluble powder, which when allowed to remain several days in methyl alcohol with concentrated sulphuric



acid slowly dissolves and is converted into *dimethyl 3-chlorophenylglycine-2-carboxylate* (annexed formula), prisms, m. p. 55–56°.


 $\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$

6-Chloroanthranilic acid on treatment with carbonyl chloride yields *6-chloroisatoic anhydride*, sparingly soluble leaflets, decomposing at about 280°, which on esterification is converted into *methyl 6-chloroanthranilate*,  $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CO}_2\text{Me}$ , a pale yellow oil, b. p. 156–158°/10 mm. F. M. G. M.

**Mono- and Di-ethyl Esters of Diphenylitaconic Acid.** HANS STOBBE (*Ber.*, 1911, 44, 1297–1300).— $\alpha$ -Ethyl  $\beta$ -hydrogen  $\gamma$ -diphenylitaconate,  $\text{CPh}_2\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , prepared by boiling diphenylitaconic anhydride with alcohol, has m. p. 130–131°; when treated with bromine, it yield  $\beta$ -bromo- $\gamma$ -diphenylparaconic acid. It differs from the corresponding  $\alpha$ -ester (Abstr., 1899, i, 900) in being more sparingly soluble in water, and in crystalline form; the  $\alpha$ -ester forms rhomboidal plates, whilst the  $\beta$ -ester crystallises in monoclinic needles. Improvements in the method of preparation of the  $\alpha$ -ester and of ethyl  $\gamma$ -diphenylitaconate are also described. F. B.

**Methyl Phenyliminomalonate and its Reactions.** RICHARD S. CURTISS and F. GRACE C. SPENCER (*J. Amer. Chem. Soc.*, 1911, 33, 985–992).—It has been shown in an earlier paper (Abstr., 1909, i, 764) that when methyl anilinoartartrate is treated with phosphoric oxide, it is converted into methyl phenyliminomalonate,  $\text{NPh}\cdot\text{C}(\text{CO}_2\text{Me})_2$ .

The compound is thus obtained as a thick, yellow oil; it reacts vigorously with water, alcohols, ammonia, hydrogen chloride, amines, and acids, with formation of colourless, substituted anilinoimalonates. The reactivity of this substance is shown to be analogous to that of phenylcarbimide.

When methyl phenyliminomalonate is treated with aniline, methyl dianilinomalonate (Courad and Reinbach, Abstr., 1902, i, 211) is produced. This compound can also be obtained by the action of aniline on methyl dihydroxymalonate.

Methyl phenyliminomalonate absorbs water from the air, thereby becoming converted into a mixture of methyl dianilinomalonate and methyl dihydroxymalonate.

It has been shown previously (Curtiss, Abstr., 1897, i, 556) that when a solution of ethyl anilinomalonate in light petroleum is heated with freshly precipitated mercuric oxide, the latter undergoes reduction and ethyl dianilinomalonate is produced. It has now been found that when methyl anilinomalonate is treated similarly, the reduction of the mercuric oxide proceeds more slowly and less completely, and a mixture of methyl dihydroxymalonate and dianilinomalonate is produced.

When dry ammonia is passed into an ethereal solution of methyl phenyliminomalonate, a white, crystalline compound and a red, gummy substance are formed. The former is very unstable, and seems readily to undergo polymerisation. Hydrogen chloride reacts with methyl phenyliminomalonate with production of an unstable, crystal-

line compound, which rapidly loses hydrogen chloride on exposure to the air, and changes into gummy polymerisation products. This polymerisation of methyl phenyliminomalonate appears to be analogous to that of phenylcarbimide.

By the action of ethyl alcohol on methyl phenyliminomalonate, a colourless, crystalline compound, m. p.  $88^{\circ}$  (uncorr.), probably  $\text{OEt}\cdot\text{C}(\text{CO}_2\text{Et})_2\cdot\text{NHPh}$ , is produced, which gradually becomes yellow when left in a desiccator.

E. G.

**Position of the Substituents in  $\alpha$ -Resodicarboxylic Acid.** PAUL WAITZ (*Monatsh.*, 1911, 32, 427—434).—The identification of Senhofer and Brunner's  $\alpha$ -resodicarboxylic acid as 2:6 dihydroxybenzene-1:3-dicarboxylic acid has been achieved: (1) by heating  $\beta$ - and  $\gamma$ -resorecylic acids separately with ammonium carbonate and water at  $130^{\circ}$  in closed vessels, whereby  $\alpha$ -resodicarboxylic acid is obtained in each case; (2) by heating  $\alpha$ -resodicarboxylic acid with water in sealed tubes, whereby it is decomposed into carbon dioxide and  $\beta$ - and  $\gamma$ -resorecylic acids.

C. S.

**Derivatives of Nitrohemipinic Acid.** RUDOLF WEGSCHEIDER and ALFONS KLEMENC (*Monatsh.*, 1911, 32, 377—401).—Since boiling aniline hydrolyses nitrated phenolic ethers (Abstr., 1910, i, 670), its action on nitrohemipinic acid has been examined. After one hour methylaniline and a substance insoluble in concentrated potassium hydroxide are obtained as by-products, the chief product being 6-nitromethylnorhemipin-2-anilic acid (6-nitro-3-hydroxy-4-methoxyphthal-2-anilic acid),  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}(\text{NO}_2)(\text{OH})(\text{OMe})\cdot\text{CO}\cdot\text{NHPh}$ , microscopic prisms, m. p.  $163$ — $184^{\circ}$  (decomp.); occasionally the substance merely darkens at  $180^{\circ}$ , and melts without decomposition at  $214^{\circ}$ , due probably to the formation of the anil (see below). The anilic acid behaves as a dibasic acid, forms blood-red solutions in alkalis, and does not give a colour reaction with ferric chloride. It yields nitromethylnorhemipinic acid when boiled with water, and forms a disilver salt, which is converted by methyl iodide into methyl 6-nitrohemipin-2-anilate,  $\text{C}_{17}\text{H}_{16}\text{O}_7\text{N}_2$ , m. p.  $148$ — $149^{\circ}$ .

A moist ethereal solution of acetylnitromethylnorhemipinic anhydride (see below) and aniline, after two hours' boiling, yields yellow needles of a mixture, m. p.  $197$ — $198^{\circ}$ , of the aniline salts of 6-nitromethylnorhemipin-1-anilic acid and its acetyl derivative. The same mixture, which is also produced by working in benzene or without a solvent, yields 6-nitromethylnorhemipin-1-anilic acid by treatment with potassium hydroxide and subsequent acidification of the red solution. The acid has m. p.  $192^{\circ}$  (decomp.), resolidifies, and melts again at  $213^{\circ}$ , the m. p. of the anil below. It differs from the preceding isomeride in behaving as a monobasic acid, and in developing a ruby-red coloration with ferric chloride, a sign that the hydroxyl and carboxyl groups are in the ortho-position to one another. 6-Nitromethylnorhemipin-1-anilic acid forms a sparingly soluble ammonium salt, m. p.  $229$ — $230^{\circ}$  (decomp.), a silver salt, and a disilver salt; from the two silver salts methyl iodide produces methyl 6-nitromethylnorhemipin-1-anilate, m. p.  $192$ — $193^{\circ}$  (decomp.), and methyl 6-nitrohemipin-1-anilate, m. p.  $170^{\circ}$

(decomp.), respectively, neither of which gives a colour reaction with ferric chloride.

The following facts prove that 6-nitromethylnorhemipin-1-anilic acid and 6-nitromethylnorhemipin-2-anilic acid are derived from the same nitromethylnorhemipinic acid. (i) Both yield the same 6-nitro-

*methylnorhemipinanil*,  $\text{NO}_2 \cdot \text{C}_6\text{H}(\text{OH})(\text{OMe}) \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{NPh}$ , m. p.

214—215°, when heated in boiling xylene. The anil, which does not give a ferric chloride reaction, is also obtained by heating methyl 6-nitromethylnorhemipin-1-anilate at 198°, or by boiling nitromethylnorhemipinic acid with aniline. (ii) Both react with acetic anhydride and two drops of sulphuric acid on the water-bath to form nitromethylnorhemipinic acid and the acetylated *anil*,  $\text{C}_{17}\text{H}_{13}\text{O}_3\text{N}_2$ , m. p. 212—213°, the latter of which is also produced by acetylating nitromethylnorhemipinanil under the preceding conditions. The hydrolysis of the acetylated anil by aqueous potassium hydroxide (2 mols.) yields 6-nitromethylnorhemipin-2-anilic acid (this is evidently a method whereby 6-nitromethylnorhemipin-1-anilic acid can be converted through the acetylated anil into the isomeric 2-anilic acid, and yields a purer product than the method described above); when hydrolysed by 1 mol. of potassium hydroxide, the acetylated anil yields 6-nitromethylnorhemipinic acid identical with that obtained from nitromethylnorhemipinic acid by Elbel or by the nitration of methylnorhemipinic acid.

6-Nitromethylnorhemipinic acid is obtained best by passing hydrogen chloride for fifteen hours through a mixture of nitrohemipinic acid and concentrated hydrochloric acid on the water-bath. It has m. p. 205—206° (decomp.) (Elbel gives 220°), and its silver salt and methyl iodide yield *dimethyl 6-nitromethylnorhemipinate*, m. p. 145—146°, which contains a free hydroxyl group, but does not give a coloration with ferric chloride. The acid is not acetylated by acetic anhydride and sodium acetate or 2 drops of sulphuric acid, but is converted by boiling acetyl chloride into *acetylnitromethylnorhemipinic anhydride*,  $\text{C}_{11}\text{H}_7\text{O}_3\text{N}$ , m. p. 165—166°, which is easily hydrolysed to nitromethylnorhemipinic acid by boiling water. C. S.

**Methylenedisalicylic Acid [Methanedisalicylic Acid] and its Reaction with Bromine and Iodine.** ERIC CLEMMENSEN and ARNOLD H. C. HEITMAN (*J. Amer. Chem. Soc.*, 1911, 33, 733—745).—Methanedisalicylic acid was first prepared by Geigy (D.R.P. 49970) by heating salicylic acid with a large excess of formaldehyde in presence of concentrated hydrochloric acid, and was afterwards studied by Kahl (Abstr., 1898, i, 259) and Madsen (Abstr., 1907, i, 424). It is now shown that the acid can be obtained in good yield by the interaction of formaldehyde (1 mol.) with salicylic acid (1 mol.) in presence of 50% sulphuric acid. If the reaction is carried out in very concentrated solution, a *compound* is produced which has the same empirical formula as methanedisalicylic acid, and does not melt but chars above 260°. When methanedisalicylic acid is heated either above its m. p. or with potassium hydroxide, it is decomposed into hydroxyphenylmethanedisalicylic acid, 4:4'-dihydroxydiphenylmethane,

and carbon dioxide. Calcium, dicalcium, barium, di-barium, magnesium, and zinc methanedisalicylates are described. The di-acetyl derivative, m. p. 142°, forms a white, amorphous powder.

Hydroxyphenylmethanedisalicylic acid (hydroxyphenylhomosalicylic acid),  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{H}$ , m. p. above 60°, is a pale red, amorphous substance.

The following compounds were obtained by the action of bromine and iodine respectively on methanedisalicylic acid in presence of alkali hydroxide.

Tribromoanthratriquinonedihomosalicylic acid,  $\text{C}_{30}\text{H}_{13}\text{O}_8\text{Br}_3$ , is a red, amorphous substance, which decomposes above 200°; its calcium salt,  $\text{C}_{30}\text{H}_{11}\text{O}_{10}\text{Br}_3\text{Ca}$ , and potassium salt,  $\text{C}_{30}\text{H}_9\text{O}_{10}\text{Br}_3\text{K}_4$ , are described.

Tri-iodoanthratriquinonedihomosalicylic acid,  $\text{C}_{30}\text{H}_{13}\text{O}_8\text{I}_3$ , is a red substance which decomposes above 230°; its calcium salt,  $\text{C}_{30}\text{H}_{11}\text{O}_{10}\text{I}_3\text{Ca}$ , and potassium salt,  $\text{C}_{30}\text{H}_9\text{O}_{10}\text{I}_3\text{K}_4$ , were prepared. When this acid is

heated in a sealed tube with 1% alkali carbonate or 2% mineral acid, it is converted into a monocarboxylic acid, which may be regarded as a tri-iodo-derivative of hydroxybenzylideneanthratriquinonehomosalicylic acid (annexed formula).

Heptabromoanthratriquinonedihomosalicylic acid,  $\text{C}_{30}\text{H}_9\text{O}_8\text{Br}_7$ , forms a pale yellow powder and decomposes above 200°; its potassium salt,  $\text{C}_{30}\text{H}_7\text{O}_{10}\text{Br}_7\text{K}_4$ , is described.

Pentabromohydroxybenzylideneanthratriquinonehomosalicylic acid,  $\text{C}_{30}\text{H}_{11}\text{O}_8\text{Br}_5$ , crystallises in microscopic plates.

Pentaiodohydroxybenzylideneanthratriquinonehomosalicylic acid,  $\text{C}_{30}\text{H}_{11}\text{O}_8\text{I}_5$ ,

is a reddish-yellow, amorphous substance; its potassium salt,  $\text{C}_{30}\text{H}_9\text{O}_{10}\text{I}_5\text{K}$ , forms an olive-green powder.

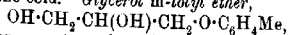
When tribromoanthratriquinonedihomosalicylic acid is boiled with potassium hydroxide solution and zinc dust, it is converted into

anthratriquinonedihomosalicylic acid (annexed formula), which forms a brown powder, and decomposes at 185°; the

calcium salt,  $\text{C}_{30}\text{H}_{11}\text{O}_{10}\text{Ca}$ , and potassium salt,  $\text{C}_{30}\text{H}_{12}\text{O}_{10}\text{K}_4$ , are described; the ethyl ester forms a colourless, amorphous, resinous mass, and yields a hexa-acetyl derivative, m. p. above 70°.

E. G.

Derivatives of Amino-acids. IV. Compounds with Glycerol. EMIL ABDERHALDEN and LOUIS BAUMANN (*Zeitsch. physiol. Chem.*, 1911, 72, 50—57. Compare Abderhalden and Guggenheim, *Abstr.*, 1910, i, 226).—Glycerol monotyrosine forms a crystalline copper salt,  $\text{C}_{24}\text{H}_{32}\text{O}_{10}\text{N}_2\text{Cu}$ , which gives a red coloration with Millon's reagent even in the cold. Glycerol m-tolyl ether,



crystallises in long, rectangular plates, m. p. 65—70° (corr.), and

*glycerol chloro-m-tolyl ether*,  $C_{10}H_{13}O_2Cl$ , crystallises from benzene in groups of needles, m. p.  $90^\circ$  (corr.).

*Glyceroldityrosine*,  $OH \cdot CH[CH_2 \cdot O \cdot C_6H_4 \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H]_2$ , obtained by the action of glyceryl- $\alpha$ -dichlorohydrin on the sodium derivative of tyrosine, has not been obtained in a crystalline form. It has m. p.  $275^\circ$  (corr.) (decomp.), and yields a copper salt,  $C_{21}H_{24}O_7N_2Cu$ .

*Glycerol di-glycyl-L-tyrosine*,

$OH \cdot CH[CH_2 \cdot O \cdot C_6H_4 \cdot CH_2 \cdot CH(CO_2H) \cdot NH \cdot CO \cdot CH_2 \cdot NH_2]_2$ , prepared by the action of glyceryl- $\alpha$ -dichlorohydrin on the sodium derivative of glycyl-L-tyrosine, is precipitated by the addition of alcohol to its aqueous solution, has m. p.  $210^\circ$  and  $[\alpha]_D^{20} + 25.3^\circ$  in 5% hydrochloric acid. An isomeride, which is sparingly soluble in water, has m. p.  $248^\circ$  and  $[\alpha]_D^{20} + 36.6^\circ$  in 5% hydrochloric acid.

*Glyceryltrityrosine*,  $C_9H_{10}O_2N \cdot O \cdot CH[CH_2 \cdot O \cdot C_6H_4 \cdot O_2N]_2$ , crystallises in minute needles, m. p.  $295^\circ$  (corr.). The hydrochloride of the ethyl ester,  $C_{28}H_{47}O_5N_3Cl$ , is hygroscopic, and has m. p.  $83^\circ$ . J. J. S.

*N-Phenyl Ethers of the Oximes.* ANGELO ANGELI, LUIGI ALESSANDRI, and M. AIAZZI-MANCINI (*Atti R. Accad. Lincei*, 1911,

[v], 20, i, 546—555).—The formula  $R \cdot CH \cdot \begin{smallmatrix} NR \\ \diagdown \\ O \end{smallmatrix}$ , which is usually

ascribed to the *N*-alkylated aldioximes, does not explain the instability of these compounds towards permanganate, to which the oxides,

$R \cdot CH \cdot \begin{smallmatrix} CHR \\ \diagdown \\ O \end{smallmatrix}$ , are stable. It is, further, not in accord with the

observation that, in all the more definite and more gentle transformations which these compounds undergo, the oxygen atom is always obtained united with the nitrogen, never with the carbon atom. The authors therefore suggest the formula  $R \cdot CH \cdot NR \cdot O$ , which is supported by the failure of Scheiber (this vol., i, 382) to prepare these compounds in optically active modifications.

It is found that the action of magnesium phenyl bromide or iodide on the *N*-phenyl or *N*-benzyl derivative of benzaldoxime proceeds according to the scheme:  $CHPh : NPh : O \rightarrow CHPh_2 \cdot NPh \cdot OH$ , and is hence analogous to the reaction which takes place with benzylideneaniline:  $CHPh : NPh \rightarrow CHPh_2 \cdot NPh$  (compare Busch, *Abstr.*, 1904, i, 663).

$\beta$ -Phenyl- $\beta$ -diphenylmethylhydroxylamine,  $CHPh_2 \cdot NPh \cdot OH$ , forms colourless prisms, m. p.  $127^\circ$ , and becomes yellow in the light. When oxidised by means of mercuric oxide, benzaldehyde or magnesium phenyl bromide, it is partly converted into the compound,  $C_{19}H_{15}ON$ , which forms pale yellow leaflets, m. p.  $214^\circ$ , and is also obtained in small proportion in the preparation of the triphenylmethylhydroxylamine. When oxidised with chromic acid, either of these compounds yields nitrosobenzene and benzophenone, whilst, on reduction, diphenylanilinomethane (compare Busch, *loc. cit.*) is obtained. Reduction of the *N*-phenyl derivative of benzaldoxime by means of zinc and ammonium chloride, yields benzylideneaniline; under the same conditions the compound, m. p.  $214^\circ$ , gives a substance, m. p.  $83^\circ$ , having

the same composition as benzophenoneaniline, but differing from it somewhat in its characters.

Oxidation of  $\beta$ -dibenzylhydroxylamine by means of mercuric oxide yields the *N*-benzyl derivative of benzaldoxime, and the action on this of magnesium phenyl bromide gives  $\beta$ -benzyl- $\beta$ -diphenylmethylhydroxylamine,  $\text{CHPh}_2\text{N}(\text{CH}_2\text{Ph})\cdot\text{OH}$ , forming white crystals, m. p.  $105^\circ$ ; on oxidation with mercuric oxide, the latter gives a compound,  $\text{C}_{20}\text{H}_{17}\text{ON}$ , m. p.  $159^\circ$ , which yields benzaldehyde and benzophenone on treatment with chromic acid.

T. H. P.

Action of Acid Chlorides and Anhydrides and of Ketones on the Sodium Derivative of Phenylacetonitrile. FERNAND BODROUX (*Compt. rend.*, 1911, 152, 1594—1596. Compare Abstr., 1910, i, 257, 482, 557, 622, 623).—The sodium derivative of phenylacetonitrile reacts normally with acetyl chloride or acetic anhydride, giving poor yields of  $\alpha$ -cyanobenzyl methyl ketone. Benzoyl chloride gives a 95% yield of the corresponding ketone, but phthalic anhydride is without action.

Double decomposition occurs when aliphatic ketones react with the sodium derivative, and the original substances are regenerated on treating the product with water. In the case of the aromatic ketones, however, a molecule of sodium hydroxide is eliminated; thus benzophenone gives  $\alpha\beta$ -diphenylcinnamonitrile; phenyl *p*-tolyl ketone forms  $\alpha$ -phenyl- $\beta$ -*p*-tolylcinnamonitrile,  $\text{CN}\cdot\text{CPh}\cdot\text{CPh}\cdot\text{C}_6\text{H}_4$ , needles, m. p.  $123^\circ$ ;  $\alpha$ -naphthyl phenyl ketone gives  $\alpha$ -phenyl- $\beta$ - $\alpha$ -naphthylcinnamonitrile, small prisms, m. p.  $174$ — $175^\circ$ .

W. O. W.

New Method for Obtaining  $\beta$ -Diketones. ÉMILE ANDRÉ (*Compt. rend.*, 1911, 152, 1488—1490. Compare this vol., i, 268).—The additive compounds formed by the union of amines with acetylenic ketones behave towards acids in the same way as Moureau and Lazennec's  $\beta$ -aminonitriles (Abstr., 1906, i, 956), giving rise to  $\beta$ -diketones and the salt of an amine. A number of diketones, such as acetylacetophenone and dibenzoylmethane, are readily prepared in this way.

W. O. W.

Metallic Compounds of Diaryl Ketones. WILHELM SCHLENK and THOMAS WEICKEL (*Ber.*, 1911, 44, 1182—1189).—From the observations of Beckmann and Paul (Abstr., 1892, 169) on the sodium derivatives of diaryl ketones, the authors were led to the conclusion that these compounds contained tervalent carbon, and, in order to support this view, have prepared and examined the chemical behaviour of several new representatives.

*p*-Phenylbenzophenone (phenyl diphenyl ketone) and di-*p*-phenylbenzophenone (di-diphenyl ketone) combine with sodium in benzene or ethereal solution, yielding strongly coloured sodium compounds containing one molecule of ketone combined with one atom of sodium; similar potassium compounds have also been prepared. The sodium derivative of di-*p*-phenylbenzophenone, when exposed to air in ethereal solution, at once loses its deep green colour with the formation of sodium peroxide and the original ketone. It readily reacts with

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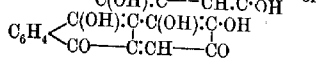
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hor has conducted experiments with hydroxyanthraquinones to obtain the relation between the constitution of a dye and its power forming lakes with mordants. The following deductions are an amplification of those already recorded.

Firstly, the influence of hydroxyl groups on the colour of the lakes of hydroxyanthraquinones. Hydroxyl groups in the  $\alpha$ -positions produce red and blue dyes, in the  $\beta$ -positions yellow and brown dyes; however, an  $\alpha$ -hydroxyl group may mask the effect of a  $\beta$ -hydroxyl group, and vice versa. Thus the colour of the lakes of the 1:2:5-, 1:2:6-, 1:2:7-, and 1:2:8-trihydroxyanthraquinones do not differ materially from those of the lakes of alizarin itself. Anthragallol (2:3-trihydroxyanthraquinone), however, forms brown lakes and so does  $\beta$ -oxyanthragallol, whilst 1:2:3:4-tetrahydroxyanthraquinone, under the influence of the new  $\alpha$ -hydroxyl group, again forms red lakes. In fact, the distinction is so sharp between alizarin (and the dyeing trihydroxyanthraquinones which produce yellow or brown colorations, that a difference in the constitutions of members of two groups must be conceded. The hydroxyanthraquinones, therefore, are divisible into two groups. One group, comprising anthracol,  $\beta$ -hydroxyanthragallol, xanthopurpurin, anthrachryson, ruficol, 1:6- and 1:7-dihydroxyanthraquinone, and other derivatives giving yellow and brown lakes, has a para-quinonoid structure; for example, anthragallol,  $C_6H_4$   $\begin{matrix} \diagup \text{CO} \text{---} \text{C} \cdot \text{C}(\text{OH}) \cdot \text{CO} \\ \diagdown \text{C}(\text{OH}) \cdot \text{C} \text{---} \text{CH} \cdot \text{C} \cdot \text{OH} \end{matrix}$  or



with the other group, which includes alizarin and its derivatives giving red or blue lakes (except hystazarin, which occupies an intermediate position), has an ortho-quinonoid structure; for example, alizarin,  $C_6H_4$   $\begin{matrix} \diagup \text{C}(\text{OH}) \cdot \text{C} \cdot \text{CO} \cdot \text{C} \cdot \text{OH} \\ \diagdown \text{CO} \text{---} \text{C} \cdot \text{CH} \cdot \text{CH} \end{matrix}$ .

In individual hydroxyanthraquinones the tendency to the production of one or other of the quinonoid forms may be such that one and the same dye may be ortho-quinonoid in some of its lakes and para-quinonoid in others; by this is an explanation is found of the fact that, for example, 1:6-dihydroxyanthraquinone, which usually yields yellow or brown lakes, produces a strong red tone with a chromium mordant.

With respect to the relation between the positions of the hydroxyl groups and the lake-forming power of the dye, the introduction of a new hydroxyl group into a hydroxyanthraquinone may increase or diminish its power of producing lakes. Thus 1:2:8-trihydroxyanthraquinone forms lakes more readily than alizarin, whilst 1:5:8-tetrahydroxyanthraquinone has very little lake-forming power in comparison with 1:4:5-trihydroxyanthraquinone. Octahydroxyanthraquinone has been prepared (following abstract) and found to exhibit a lake-forming power scarcely more pronounced than that of quinizarin (1:4-dihydroxyanthraquinone). This discovery destroys the tenability of Liebermann and Kostanecki's rule; it is, however, that those members of the hydroxyanthraquinones

which contain hydroxyl groups in the ortho-position are the most pronounced mordant dyes.

Mohlau has disputed the author's statement that hystazarin (2:3-dihydroxyanthraquinone) is a more pronounced mordant dye than 1:3- or 1:4-dihydroxyanthraquinone; in reply, the author shows that quinizarin hardly dyes wool mordanted with tin, whilst hystazarin produces a full orange tone which is fast to milling.

C. S.

**Octahydroxyanthraquinone.** GEORG VON GEORGIEVICS (*Monatsh.*, 1911, 32, 347—352).—Three parts of rufgallol (1:2:3:5:6:7-hexahydroxyanthraquinone), 100 parts of sulphuric acid ( $H_2SO_4$ ,  $H_2O$ ), 4 parts of boric acid, and about 0.05 part of mercuric oxide are heated at 250—260° until a drop of the mixture dissolves in concentrated sulphuric acid with a pure blue colour; the yield of the octahydroxyanthraquinone diminishes rapidly when the heating is too prolonged. The reddish-brown precipitate obtained by pouring the cold mixture into water is washed with boiling water, dried, and crystallised by treating its boiling, saturated solution in pyridine with boiling methyl alcohol and a little water, whereby the dye is obtained in stout, brownish-red needles. *Octahydroxyanthraquinone* can only be crystallised from pyridine or methyl alcohol, yields anthracene by distillation with zinc dust, forms an *octa-acetate*, pale yellow needles, decomp. about 200°, and dissolves in concentrated sulphuric acid, forming a greenish-blue solution (the presence of a red tinge indicates the presence of rufgallol). Its behaviour as a mordant dye has been described (preceding abstract).

C. S.

**Preparation of Anthraquinonylglycines.** FARBWERKE VON MEISTER, LUCIUS & BRÜNING (D.R.-P. 232127).—Anthraquinonylglycines may readily be obtained by the action of glyoxylic or thio-glyoxylic acid on the corresponding reduced aminoanthraquinones.  *$\beta$ -Anthraquinonylglycine*, orange-yellow crystals, m. p. 236°, is prepared by reducing  $\beta$ -aminoanthraquinone with sodium hyposulphite in aqueous alkaline solution, with the subsequent addition of an alkali glyoxylate and heating during one hour. Unchanged  $\beta$ -aminoanthraquinone is separated by a current of air, and the product precipitated by the addition of mineral acid.

*$\alpha$ -Anthraquinonylglycine* forms red crystals, m. p. 262° (decomp.).

F. M. G. M.

**Desiccation of *cis*-Terpin Hydrate.** A. LEULIER (*J. Pharm. Chim.*, 1911, [vii], 3, 440—441).—When terpin hydrate is dried at 100°, part of the terpin formed is volatilised, consequently desiccation should be effected by exposure at atmospheric temperature over sulphuric acid under reduced pressure.

T. A. H.

**Sesquiterpene and an Olefinic Camphor Occurring in Southern Cypress.** ALLAN F. ODELL (*J. Amer. Chem. Soc.*, 1911, 33, 755—758).—During the course of some work on the oxidation of

press (*Taxodium distichum*) sawdust, a fragrant odour was observed, and the present investigation was therefore undertaken.

On extracting cypress sawdust with alcohol, and removing the latter by distillation, a red, viscous product was obtained. By the fractional distillation of this extract under reduced pressure, two new compounds were isolated.

*Cypressene*,  $C_{15}H_{24}$ , b. p. 218–220°/35 mm., and 295–300°/778 mm., a yellowish-green, viscous, nearly odourless liquid, which has  $D_4^{25}$  0.9647,  $n_D^{25}$  1.5240,  $[\alpha]_D^{25} + 6.53^\circ$ , reacts violently with moderately strong nitric acid to form a yellow, amorphous oxidation product, and gives a red coloration with concentrated sulphuric acid. The compound contains only one ethylene linking, and is therefore a triyclic sesquiterpene.

The other new compound, *cypreal*,  $C_{12}H_{20}O$ , is probably an aldehyde. It was obtained as a pale yellow, fragrant, mobile liquid, which has b. p. 182–185°/35 mm.,  $D_4^{20}$  0.9469,  $n_D^{20}$  1.5040, is dextrorotatory, and readily reduces ammoniacal solution of silver nitrate. E. G.

**Humulene of Oil of Hop Flowers.** ERNST DEUSSEN (*J. pr. chem.*, 1911, [ii], 83, 483–489).—Humulene, b. p. 118–119°/10 mm., obtained from oil of hop flowers by fractional distillation, has been identified with *i*- $\alpha$ -caryophyllene (Abstr., 1908, i, 353; 1909, i, 171, 13) by a comparison of the nitrosates and nitrosochlorides. C. S.

**Essential Oil of the Dwarf Pine.** ERICH BÜCKER and ALFRED LAHN (*J. pr. Chem.*, 1911, [ii], 83, 489–498).—The oil of the dwarf pine (*Pinus pumilo*), freed from terpenes and sesquiterpenes, and having  $D_4^{15}$  0.8707,  $[\alpha]_D - 9.45^\circ$ , and esterification number 13.4, has been examined with respect to its oxygenated constituents. In addition to *l*-bornyl acetate, it contains aldehydic and ketonic substances, and at least 30% of alcohols and esters of the terpene and sesquiterpene series, as yet unexamined.

The oil has been separated into twelve fractions boiling between 5° and 178°/13 mm. The fractions are dissolved separately in 96% alcohol, and shaken for two to three hours with 30% aqueous sodium hydrogen sulphite. The fraction, b. p. 148–160°/13 mm.,  $[\alpha]_D - 14.15^\circ$ , esterification number 53, gives by this treatment a small yield of a hydrogen sulphite compound, which after hydrolysis yields an oil,  $C_{15}H_{24}O$ , which is unsaturated and restores the colour of Schiff's reagent. The fractions b. p. 138–148°/13 mm. and 127–138°/13 mm. are united and distilled; the portion b. p. 128–135°/15 mm. yields a hydrogen sulphite compound, from which, by hydrolysis, is obtained a substance,  $C_{15}H_{24}O$ , which is levorotatory, unsaturated, and probably of ketonic nature.

The fractions b. p. 105–109°, 109–113°, 113–118°, and 118–127°, all under 13 mm., do not yield hydrogen sulphite compounds, but contain *l*-bornyl acetate.

The fractions b. p. 85–100°/13 mm. and 100–105°/13 mm. differ from all the others by having an intense, peculiar odour. By combining them and distilling, a portion b. p. 87–95°/14 mm. is obtained, which yields a white, crystalline hydrogen sulphite com-

pound. The substance,  $C_8H_{14}O$ , obtained by the hydrolysis of this compound by 20% sodium carbonate, has ketonic properties, and is called *pumilone*. It has b. p. 216—217°/754 mm.,  $D^{20}_D$  0.9314,  $D^{20}_D$  0.9238,  $n_D^{20}$  1.46459, and  $[\alpha]_D^{20}$  -15°. It has a very intense, not unpleasant odour. The odour of the natural dwarf pine oil is mainly due to pumilone, although it is present only to the extent of 1—2%. Pumilone, which is unsaturated and contains one double linking, does not yield characteristic derivatives, except the hydrogen sulphite compound and the *semicarbazone*, m. p. 116—117°. C. S.

**Theory of the Vulcanisation of Caoutchouc.** F. WILLY HINRICHSSEN (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 245—250. Compare Abstr., 1910, i, 330).—The influence of time on the proportion of free sulphur in a sample of vulcanised para-rubber has been examined. The total and free sulphur were estimated in the original material, of which samples were kept for six months under different conditions. The experimental data show that the proportion of free sulphur diminishes with time, and that the rate of diminution is much greater at 70° than at room temperature. These observations agree with the author's view, that the sulphur present in the vulcanised caoutchouc is partly adsorbed, the remainder being chemically combined. The adsorption equilibrium is attained very quickly, but the chemical action at low temperatures is relatively a very slow process. As the chemical reaction proceeds, the proportion of free sulphur gradually diminishes. H. M. D.

**Cold Vulcanisation.** F. WILLY HINRICHSSEN (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 250—251).—Polemical against Bysoff (compare this vol., i, 390). H. M. D.

**Properties of Dammar Resins.** CHARLES COFFIGNIER (*Bull. Soc. chim.*, 1911, [iv], 9, 549—561. Compare Abstr., 1902, i, 533).—The solubilities and analytical constants of some commercial dammar resins are recorded.

Dammar resin from Padang has  $D^{18}_D$  1.036, m. p. 95°, acid number 31.4, and saponification number 33.7; that from Borneo has  $D^{18}_D$  1.043, m. p. 120°, acid number 35.1, and saponification number 64.5. Singapore Dammar has  $D^{18}_D$  1.057, m. p. 95°, acid number 30.1, and saponification number 39.3. Pontianac Dammar has  $D^{18}_D$  1.025, m. p. 110°, acid number 19.9, and saponification number 30.9. Sumatra Dammar has  $D^{18}_D$  1.004, m. p. 190°, acid number 59.6, and saponification number 64.5. Batjan Dammar has  $D^{18}_D$  1.032, m. p. 105°, acid number 18.5, and saponification number 19.6. The solubilities of these dammars in twelve solvents are recorded, and similar data for a number of solvents are given in the cases of Batavian dammar, sandarac, and mastic resins. T. A. H.

**Constitution of Bixin.** J. F. B. VAN HASSELT (*Rec. trav. chim.*, 1911, 30, 1—47. Compare Marchlewski and Matejko, Abstr., 1906, i, 760).—The author has obtained bixin from anatto by Zwick's process (Abstr., 1900, i, 513) in large, violet, triclinic crystals, m. p.

187°. The analytical data and the molecular weight by the ebullioscopic method in chloroform point to a formula  $C_{30}H_{44}O_5$ . Etti and Zwick describe mono- and di-potassium derivatives of bixin, and therefore consider that bixin behaves like a dibasic acid. This is not so, the di-potassium compound being a derivative of a new substance, called norbixin, obtained from bixin by the substitution of its methoxyl methyl group by potassium. When bixin is dissolved in boiling aqueous potassium hydroxide, methyl alcohol is evolved, and is detected as formaldehyde after oxidation; by acidifying the alkaline solution, *norbixin*,  $C_{28}H_{32}O_5$ , is precipitated. It is a light red, crystalline powder, decomp. 240°, and is insoluble in chloroform.

When a solution of bixin (or of purified anatto) and an equivalent amount of potassium hydroxide, dissolved in boiling methyl alcohol, are treated first with ethyl acetate and then with methyl sulphate and a little potassium hydroxide, *bixin methyl ether*,  $C_{30}H_{36}O_5$ , m. p. 156°, is obtained. It crystallises in red, pleochroic rhomboids, develops an intense blue coloration with concentrated sulphuric acid, and is hydrolysed by alcoholic potassium hydroxide, yielding *norbixin*. (*bixin ethyl ether*,  $C_{31}H_{38}O_5$ , m. p. 138°, prepared in a similar manner, forms violet crystals.) By treatment with methyl sulphate, *norbixin* yields bixin and bixin methyl ether. Bixin contains one methoxy-group, bixin methyl ether two, and *norbixin* none.

The preceding transformations show that the relation between *norbixin*, bixin, and bixin methyl ether is expressed by the formulæ  $OH \cdot R \cdot OH$ ,  $OH \cdot R \cdot OMe$ , and  $OMe \cdot R \cdot OMe$ , where R is  $C_{28}H_{30}O_3$ . When a solution of potassium *norbixin*, obtained by hydrolysing bixin with alcoholic potassium hydroxide, is treated with ethyl sulphate, the precipitate contains *norbixin diethyl ether*,

$C_{28}H_{30}O_3(OEt)_2$ ,  
blue rhomboids, m. p. 121°, whilst *norbixin ethyl ether*,

$C_{28}H_{30}O_3(OEt) \cdot OH$ ,  
red needles, m. p. 176°, is obtained by acidifying the mother liquor. The latter is quite analogous to bixin in its behaviour, but is more slowly hydrolysed by potassium hydroxide.

The two hydroxyl groups in *norbixin* are not symmetrically situated in the molecule, since two isomeric *norbixin methyl ethyl ethers* have been obtained. The one is bixin ethyl ether, m. p. 138°, described above; the other, *isobixin ethyl ether*, m. p. 149°, is prepared by methylating *norbixin ethyl ether*, and crystallises in large, red rhomboids. It follows, therefore, that an isomeride of bixin itself should be capable of existence. This isomeride, *isobixin*,  $OH \cdot C_{28}H_{30}O_3 \cdot OMe$ , m. p. 178°, is obtained by the partial hydrolysis of bixin methyl ether by alcoholic potassium hydroxide; its points of difference from bixin are recorded in the sequel, the most important being its stability to aqueous potassium hydroxide. When *isobixin* is treated with ethyl sulphate, *norbixin diethyl ether*, m. p. 121°, is produced, the methyl group having been ousted by an ethyl group.

The potassium derivative,  $OK \cdot C_{28}H_{30}O_3 \cdot OH$ , of bixin is easily obtained by heating a methyl-alcoholic solution of bixin just to the b. p. with an excess of potassium hydroxide; it crystallises in violet needles, and is quite insoluble in boiling water. The dipotassium

derivative of norbixin is formed when bixin is hydrolysed by aqueous or ethyl-alcoholic potassium hydroxide or by treating ethyl-alcoholic norbixin with this alkali; it forms a felted mass of reddish-brown crystals, dissolves easily in water, and oxidises readily in the air. The *disodium* derivative of norbixin and the *potassium* derivatives of norbixin, norbixin ethyl ether, and *isobixin* are also described.

The unstable orange product, m. p. 200.5°, obtained by Marchlewski and Matejko (*loc. cit.*) by reducing bixin with zinc and acetic acid, is *dihydrobixin*,  $C_{39}H_{36}O_5$ ; it is also formed when the reduction is performed in alkaline solution.

*Dihydrobixin methyl ether*,  $C_{39}H_{38}O_5$ , m. p. 174°, *dihydroisobixin*,  $C_{39}H_{36}O_5$ , m. p. 190°, and *dihydronorbixin*,  $C_{38}H_{34}O_5$ , decomp. 235°, are obtained by reducing the corresponding bixins with zinc and acetic acid; the last, however, is obtained best by reduction in alkaline solution. All of them are unstable, yellow, crystalline substances, which develop intense blue colorations with concentrated sulphuric acid.

By bromination in cold glacial acetic acid, bixin forms a *decabromide*,  $C_{39}H_{34}O_5Br_{10}$ , a white, amorphous powder, which does not develop a coloration. Four, six, or eight of the bromine atoms can be eliminated by the more or less prolonged action of zinc and dilute sulphuric acid, the products of reduction being amorphous orange substances, which give a blue coloration with sulphuric acid. Bixin-methyl ether also forms a *decabromide*,  $C_{39}H_{36}O_5Br_{10}$ , a white powder insoluble in potassium hydroxide. By treatment with iodine chloride in acetic acid, bixin, norbixin, methylbixin, and their dihydro-derivatives, and *isobixin* all combine with 10 atoms of halogen; consequently hydrogen must attack the molecule of bixin in a different manner from the halogens.

When heated by itself at 190° or in diphenylamine, bixin loses its colour and decomposes into *m*-xylene and a resinous substance, m. p. 145°, which is shown to be a mixture; *isobixin*, norbixin, the bixin-alkyl ethers, and their dihydro-derivatives also yield *m*-xylene under the same conditions.

The author is unable to confirm Zwick's statements that palmitic acid is produced by the action of steam on bixin at 160° and by the action of light on its sodium derivative. Although the behaviour of bixin with methyl sulphate indicates the presence of a hydroxyl group, attempts to acetylate or benzoylate the substance have been unsuccessful. The failure of bixin methyl ether to react with phenylhydrazine, hydroxylamine, semicarbazide, and magnesium ethyl bromide points to the absence of a carbonyl group. The action of numerous oxidising agents on bixin has been examined; characteristic products, however, have not been isolated.

C. S.

**The Chlorophyll Group. IV. Phylloporphyrin.** LÉOS MARCHLEWSKI and J. ROBEL (*Biochem. Zeitsch.*, 1911, 32, 204—221). —The authors describe various modifications of the methods published previously for preparing phylloporphyrin. The most convenient method is from a partly purified phylloaonin obtained by the method of Kőzniewski and Marchlewski. The results of detailed spectro-

scopic examination of phyllo- and meso-porphyrin are given, and also a comparison is made of the results of Willstätter and Fritzsche's porphyrins. The paper is controversial as regards the homogeneity of the products obtained by the different investigators. S. B. S.

**The Existence of Two Chlorophyllins.** LÉON MARCHLEWSKI (*Biochem. Zeitsch.*, 1911, 32, 332—333).—Controversial. Reply to Tsvett. S. B. S.

**The Solubility of the Chlorophyllins and a New Method for Isolating Them.** M. Tsvett (*Ber.*, 1911, 44, 1124—1127).—The chlorophyllins are insoluble in pure light petroleum, but dissolve readily in this solvent in the presence of a small quantity of alcohol, ether, or benzene. Substances having a similar influence on the solubility must be present in the chloroplasts, since the chlorophyllins may be extracted from the freshly-crushed leaves with pure light petroleum.

These substances may be removed by washing the petroleum solutions first with 80% alcohol and finally with water; the mixture of  $\alpha$ - and  $\beta$ -chlorophyllins then becomes insoluble, and separates out. In this manner a waxy mixture has been obtained from *Cytisus* leaves, probably identical with a substance mentioned by Willstätter and Stoll (this vol., i, 141), and having similar properties. F. B.

**Natural Dyes and Colouring Matters of the Philippines.** BENJAMIN T. BROOKS (*Philippine J. Sci.*, 1910, 5, 439—452).—Annatto, old fustic or morin, indigo, and Brazil wood are four of the principal natural dyes occurring in the Philippines which have not as yet entirely been displaced by the synthetic articles.

An alcoholic extract of narra wood, *Pterocarpus* spp., was found to contain a resin, a tannin, an amorphous, red colouring matter, two colourless, crystalline substances, and a yellow, fluorescent substance.

The red colouring matter, which is named *narrin*, swells and chars at about 180°, yields phloroglucinol and resorcinol by fusion with potassium hydroxide and vanillin by oxidation with alkaline potassium permanganate, produces a small amount of resorcinol dimethyl ether by distillation with zinc dust, and forms a brown, amorphous benzoyl derivative. A comparison of *narrin* with *santalin*, isolated from *P. santalinus*, shows that the two substances are closely related. Both are decolourised by zinc and potassium hydroxide or by sodium amalgam in dilute alcohol, yielding solutions in which the colour is restored by atmospheric oxidation; both yield potassium salts by precipitation of their alcoholic solutions by alcoholic potassium acetate. The *copper* salt of *santalin* has the formula  $\text{Cu}(\text{C}_{15}\text{H}_{13}\text{O}_5)_{1/2}$ , whilst that of *narrin* contains only 6.24% of copper. The dyeing properties of the two substances are very similar. *Narrin* is insoluble in water, but dissolves in alkaline solutions. Metallic mordants, such as chromium and copper hydroxides, are the most suitable, but the shades are not very fast to soap.

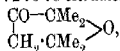
The two colourless, crystalline substances are shown to be pterocarpin and homopterocarpin. Pterocarpin has the formula  $\text{C}_{14}\text{H}_{12}\text{O}_4$ .



and m. p. 163°. Cazeneuve and Hugoncq (Abstr., 1887, 971; 1889, 160) state that it has the composition  $C_{30}H_{46}O_6$ , and m. p. 152°. Homopterocarpin,  $C_{17}H_{16}O_4$ , m. p. 86° (Cazeneuve and Hugoncq, *loc. cit.*, give  $C_{24}H_{24}O_8$ , and m. p. 82–86°), is insoluble in concentrated potassium hydroxide, but yields a little resorcinol at 200–210°. It produces resorcinol dimethyl ether by distillation with zinc dust, but does not react with phenylhydrazine or phosphorus pentachloride. Probably it is closely related to narin. C. S.

Reduction of Biliary Pigments by the Hydrogen Evolved from Palladium, Hydrogenised in Presence of Sodium Hypophosphite: Formation of Urobilinogen. JULES VILLE (*Bull. Soc. chim.*, 1911, [iv], 9, 480–483).—To a solution of pigments obtained from biliary calculi from a cow, sodium hydroxide and palladium, precipitated from the chloride by means of sodium hypophosphite, were added, and the whole warmed to 100°. Into this sodium hypophosphite solution was gradually introduced. In a short time urobilinogen was formed, and could be detected by Erlich's reagent, or by its conversion into urobilin and observation of the characteristic absorption spectrum of the latter. The reaction also takes place in the cold, but more slowly. T. A. H.

Catalytic Isomerisation of Acetylenic Pinacone [ $\beta$ -Dimethyl- $\Delta^7$ -hexinene- $\beta$ -diol]. Synthesis of 3-Keto-2:2:5:5-tetramethyl-tetrahydrofuran. GEORGES DUPONT (*Compt. rend.*, 1911, 152, 1486–1488. Compare this vol., i, 173).—When dimethyl- $\Delta^7$ -hexinene- $\beta$ -diol is heated with an aqueous solution of mercuric sulphate and the mixture distilled in steam, a mobile liquid is obtained, having a camphoraceous odour, m. p. –20.5°, b. p. 149°,  $D^{18}_4$  0.9251,  $n^{20}_D$  1.4198. This is not the expected dihydroxy-ketone, but an internal anhydride, 3-keto-2:2:5:5-tetramethyltetrahydrofuran,

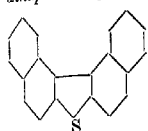


a very stable substance, yielding a *semicarbazone*, needles, m. p. 190°, an *oxime*, leaflets, m. p. 128°, and a *phenylhydrazone*, m. p. 134°. When treated with magnesium methyl bromide it forms a tertiary alcohol, m. p. 77°, identical with that obtained from  $\beta$ - $\gamma$ -trimethylhexane- $\beta$ - $\gamma$ -triol (Bouveault and Locquin, this vol., i, 2). The ketone is converted by the magnesium derivative of acetylene dibromide into a *substance*,  $C_8H_{15}O_2 \cdot C \equiv C \cdot C_8H_{15}O_2$ , m. p. 97–98°. It also behaves as an enol, giving a normal sulphate,  $(C_8H_{15}O)_2SO_4$ , m. p. 67–70°, a *sodium*, and a *potassium* salt. When the latter is treated with ethyl iodide, 3-ethoxy-2:2:5:5-tetramethyl-2:5-dihydrofuran,  $C_8H_{15}O \cdot OEt$ , is formed as a liquid, b. p. 157–159°,  $D^{18}_4$  0.8878,  $n_D^{18}$  1.4237. W. O. W.

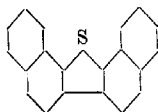
Constitution of Thiophenoquinones and Mechanism of Quinone Reactions. THEODOR POSNER (*J. pr. Chem.*, 1911, [ii], 83, 471–483).—Final reply to Michael (Abstr., 1910, i, 748) and to Michael and Cobb (*ibid.*, i, 748). C. S.

**Phenothioxin.** ENOS FERRARIO (*Bull. Soc. chim.*, 1911, [iv], 9 536—537).—There is very little interaction when sulphur and diphenyl ether are heated together, unless a catalyst, such as aluminium or magnesium chloride, is present, in which case phenothioxin (Mauthner, *Abstr.*, 1906, i, 447) is formed. Phenothioxin combines with two atoms of hydrogen when reduced, and when heated with copper at 250° forms diphenylene oxide. T. A. H.

**Dinaphthathiophen.** M. LANFRY (*Compt. rend.*, 1911, 152, 1254—1256. Compare this vol., i, 151).—From the products of the action of sulphur on naphthalene at a red heat a substance, *dinaphthathiophen*, has been isolated in the form of pearly, yellow scales,



or



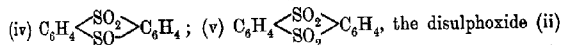
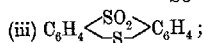
m. p. 250·5° (corr.), b. p. above 440°, without appreciable decomposition.

Its constitution is represented by the annexed formula. When the substance is oxidised

with chromic acid, it yields phthalic acid. The *hexabromo*-derivative,  $C_{20}H_6Br_6S$ , m. p. 260°, furnishes 3 : 6-dibromophthalic acid on oxidation.

Boiling nitric acid converts dinaphthathiophen into a yellow *tetra-nitro*-derivative,  $C_{20}H_6(NO_2)_4S$ , m. p. about 210°. W. O. W.

**Thianthren.** KARL FRIES and WILHELM VOGT (*Annalen*, 1911, 381, 312—337).—Of the five possible oxidation products of thianthren, namely: (i)  $C_6H_4 \begin{smallmatrix} SO \\ \diagup \quad \diagdown \\ S \end{smallmatrix} C_6H_4$ ; (ii)  $C_6H_4 \begin{smallmatrix} SO \\ \diagdown \quad \diagup \\ SO \end{smallmatrix} C_6H_4$ ;



has been recently shown (this vol., i, 395) to exist in two isomeric forms. Thianthrenmonosulphoxide (i) can be obtained by oxidising a glacial acetic acid solution of thianthren with dilute nitric acid (D 1·2) (compare Fries and Volk, *Abstr.*, 1909, i, 406). The monosulphone (iii) is formed by the action of chlorine on a boiling dilute acetic acid solution of thianthren, and when oxidised with concentrated nitric acid yields the trioxide (iv), which is also formed by the action of chlorine and water on the monosulphoxide or the isomeric disulphoxides.

Thianthren is most readily prepared by a modification of Genvresse's method (*Abstr.*, 1897, i, 240), and yields a *compound*,  $C_{12}H_8S_2, FeCl_3$ , in the form of glistening, bronzy needles, readily decomposed by water.

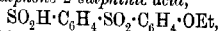
*Thianthrenmonosulphoxide*,  $C_{12}H_8OS$ , crystallises from methyl alcohol or benzene in long needles, m. p. 143°. Its solution in concentrated sulphuric acid has a brownish-red colour, which changes to a deep blue on the addition of a little water. The addition of much water precipitates the original sulphoxide, but when the solutions are kept for some time or warmed, thianthren is formed. When the

solution in concentrated hydrochloric acid is kept for some time, chloro-thianthren is deposited, but hydrogen bromide reacts with a glacial acetic acid solution of the sulfoxide, yielding thianthren. *Thianthren monosulphone*,  $C_{12}H_8O_3S_2$ , is best prepared by leading chlorine into a glacial acetic acid solution of thianthren and boiling, each operation being repeated several times. It crystallises from acetic acid in colourless, glistening plates, m. p.  $159^\circ$ , and is quite stable towards hydrogen bromide or zinc dust and acetic acid. Its solution in concentrated sulphuric acid has a rose colour, and does not decompose when kept.

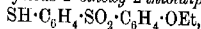
*Thianthrensulphonesulphoxide (thianthrentrioxide)*,  $C_{12}H_8O_3S_3$ , crystallises from alcohol in small, compact prisms, m. p.  $216^\circ$ ; its solution in concentrated sulphuric acid is colourless, and with hydrobromic acid it yields the monosulphone.

*Thianthren dichloride*,  $C_6H_4 \begin{smallmatrix} \text{SCl}_2 \\ \text{S} \end{smallmatrix} C_6H_4$  or  $C_6H_4 \begin{smallmatrix} \text{SCl} \\ \text{SCl} \end{smallmatrix} C_6H_4$ , obtained by the action of dry chlorine on a benzene solution of thianthren, forms brilliant red prisms, which are readily affected by moisture, yielding hydrogen chloride and the sulfoxide. When heated alone the crystals decompose into chlorine and thianthren. *4-Chlorothianthren*,  $C_{12}H_7ClS_2$ , crystallises from glacial acetic acid in prisms, m. p.  $84^\circ$ , and gives a pale violet-red coloration with concentrated sulphuric acid, but this gradually changes to a deep violet-blue. It can be prepared by the action of chlorine on a chloroform solution of thianthren and exposing the product to the action of atmospheric moisture, or from thianthren sulfoxide and an acetic acid solution of hydrogen chloride. *4:4'-Dichlorothianthren*,  $C_{12}H_6Cl_2S_2$ , obtained by the action of chlorine on thianthren or its monochloro-derivative, or by the condensation of chlorobenzene and chloride of sulphur in the presence of carbon disulphide and aluminium chloride, crystallises from benzene or glacial acetic acid in long, slender needles, m. p.  $171^\circ$ . It dissolves slowly in concentrated sulphuric acid, and the solution has a brilliant blue colour.

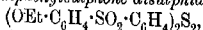
*2'-Ethoxydiphenylsulphone-2-sulphinic acid*,



obtained by boiling thianthrendisulphone (Graebe, *Annalen*, 1875, 179, 178) with alcohol and 50% potassium hydroxide solution, forms slender needles, m. p.  $151^\circ$  (decomp.), and yields a sparingly soluble sodium salt. When reduced with zinc dust and alcoholic hydrochloric acid, the sulphinic acid yields *2'-ethoxy-2-thioldiphenylsulphone*,

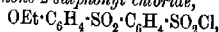


which crystallises from alcohol in small needles, m. p.  $131^\circ$ . Its solutions in alkalis are oxidised rapidly on exposure to the air. The *methyl ether*,  $C_{15}H_{10}O_3S_2$ , crystallises from benzene in compact needles, m. p.  $178^\circ$ . *2'-Ethoxydiphenylsulphone disulphide*,

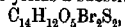


obtained by oxidising the thiol with bromine water, crystallises from glacial acetic acid in compact prisms, m. p.  $270^\circ$  (decomp.).

*2'-Ethoxydiphenylsulphone-2-sulphonyl chloride*,

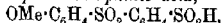


prepared by the action of chlorine on a glacial acetic acid solution of the sulphinic acid, crystallises from benzene in brilliant, compact rhombs, m. p. 159°. The corresponding *bromide*,  $C_{14}H_{13}O_3BrS_2$ , has m. p. 177°, and with excess of bromine yields a substituted *bromide*,



which crystallises in needles, m. p. 179°, and yields a *perbromide*,  $C_{14}H_{10}O_3S_4Br_4$ , in the form of orange-coloured needles. 2'-*Ethoxydiphenylsulphone-2-sulphonic acid*,  $OEt \cdot C_6H_4 \cdot SO_2 \cdot C_6H_4 \cdot SO_3H$ , crystallises from glacial acetic acid in compact needles, m. p. 178°. The corresponding *anilide*,  $C_{20}H_{19}O_3NS_2$ , crystallises in prisms, m. p. 204°.

2'-*Methoxydiphenylsulphone-2-sulphonic acid*,



obtained by hydrolysing the disulphone with methyl-alcoholic potash, has m. p. 161° (decomp.). 2'-*Methoxy-2-thioldiphenylsulphone*,



has m. p. 157°, and its *methyl ether*,  $C_{14}H_{14}O_3S_2$ , m. p. 197°. 2'-*Methoxydiphenylsulphone-2-sulphonyl chloride*,  $C_{13}H_{11}O_3ClS_2$ , forms compact prisms, m. p. 210°, and 2'-*methoxydiphenylsulphone-2-sulphonic acid*,  $C_{13}H_{12}O_6S_2$ , compact needles, m. p. 202°. The *anilide* forms rhombic crystals, m. p. 193°.

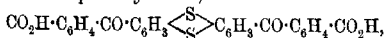
J. J. S.

Introduction of Several Phthalic Acid Groups into Aromatic Compounds. III. Experiments with Thianthren, Dimethylthianthren, Thiodiphenylamine, and *N*-Methylthiodiphenylamine. ROLAND SCHOLL and CHRISTIAN SEER (*Ber.*, 1911, 44, 1233—1249. Compare this vol. i, 452, 453).—By the action of phthalic anhydride and aluminium chloride on thianthren in the presence of carbon disulphide, thianthren-2-phthaloylic acid and the 2:6-diphthaloylic acid are formed.

The yield of the dibasic acid is increased by using more anhydride and less carbon disulphide, and heating for twenty-four hours. The mixture of the two acids can be separated by means of their ammonium salts, as the salt of the monobasic acid is sparingly, and that derived from the dibasic acid readily, soluble in water.

*Thianthren-2-phthaloylic acid*,  $CO_2H \cdot C_6H_4 \cdot CO \cdot C_6H_3 \begin{smallmatrix} \diagup S \diagdown \end{smallmatrix} C_6H_4$ , crystallises from boiling xylene, has m. p. 219—221°, and dissolves in concentrated sulphuric acid, yielding a violet-coloured solution. When heated with anhydrous zinc chloride for one hour at 230—235°, it yields 2:3-*phthaloylthianthren*,  $C_6H_4 \begin{smallmatrix} \diagup CO \diagdown \end{smallmatrix} C_6H_2 \begin{smallmatrix} \diagup S \diagdown \end{smallmatrix} C_6H_4$ , which crystallises from nitrobenzene in brilliant dark red needles, m. p. 253°. With alkaline hyposulphite it gives a dark reddish-brown solution, which does not dye unmordanted cotton.

*Thianthren-2:6-diphthaloylic acid*,



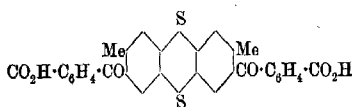
does not crystallise well, has m. p. 143—160°, and gives a dark brown coloration with concentrated sulphuric acid. When heated with

the concentrated acid for forty minutes at 120—124°, it yields 2:3:6:7-diphthaloylthianthren,



This separates from nitrobenzene in minute, brownish-red crystals, which are not molten at 325°. Its solution in concentrated sulphuric acid is grass-green, and its reduction product is dark red, but does not dye unmordanted cotton.

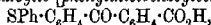
2:6-Dimethylthianthren-3:7-diphthaloylic acid (annexed formula),



prepared by heating 2:6-dimethylthianthren (Jacobson and Ney, Abstr., 1894, i, 125), phthalic anhydride, and aluminium

chloride, first at 60—100°, and then for seven hours at 100—104°, forms a light red powder, and with concentrated sulphuric acid at 120—124° yields 2:6-dimethyl-3:4:7:8-diphthaloylthianthren,  $\text{C}_{30}\text{H}_{18}\text{O}_8\text{S}_2$ , which crystallises from nitrobenzene in reddish-brown needles, m. p. 380—385° (decomp.). The vat dye obtained by the action of alkaline hyposulphite colours unmordanted cotton yellow.

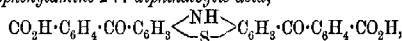
Phenylsulphidephthaloylic [phenylthiobenzoylbenzoic] acid,



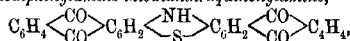
crystallises from light petroleum, and has m. p. 121—122°. The ammonium salt is sparingly soluble, and crystallises in glistening needles, m. p. 171°. When warmed at 60° with concentrated sulphuric acid it is largely sulphonated, but with zinc chloride yields phthaloylphenyl sulphide,  $\text{C}_6\text{H}_4 \cdot \text{C}_2\text{O}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SPh}$ .

Thiodiphenylamine reacts with phthalic anhydride and aluminium chloride in the presence of carbon disulphide, yielding a tribasic acid; two  $\cdot\text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$  groups are introduced into the para-positions with respect to the imino-group and meta with respect to the sulphur atom, and the third group becomes attached to nitrogen. When *N*-methylthiodiphenylamine is used, only two phthalic acid groups are introduced.

Thiodiphenylamine-2:7-diphthaloylic acid,



prepared by hydrolysing the tribasic acid with 2*N*-sodium hydroxide solution, crystallises from nitrobenzene in brick-red, glistening plates, and turns dark-coloured and decomposes at 250°. 2:3:6:7-Diphthaloylthiodiphenylamine thiodianthraquinonylamine,



obtained by heating the dibasic acid with concentrated sulphuric acid at 100—166°, crystallises from nitrobenzene, aniline or quinoline, and has m. p. 380°. It is bluish-black when dry, greenish-blue when moist, and yields a dark red vat-dye. Its sulphonic acid dyes wool a grey-green.

[With WALTER TRITSCHE.]—*N*-Methylthiodiphenylamine-2:7-diphthaloylic acid,  $\text{C}_{28}\text{H}_{18}\text{O}_8\text{NS}$ , crystallises from cumene, decomposes at

170°, and its solution in concentrated sulphuric acid has an olive-green or in thin layers a reddish-brown colour. With concentrated sulphuric acid at 100–105°, it yields 6:7-phthaloyl-N-methylthiodiphenylamine-2-phthaloylic acid,



which crystallises from nitrobenzene as a violet-black powder. 2:3:6:7-Diphtaloyl-N-methylthiodiphenylamine,  $\text{C}_{20}\text{H}_{15}\text{O}_4\text{NS}$ , crystallises from aniline in black needles, m. p. 370°, and gives a dark red vat dye.

Thio-β-dinaphthylamine also condenses with phthalic anhydride and aluminium chloride in the absence of a diluent, yielding a mixture of phthaloylic acids and thiodinaphthanthraquinoylamine, from which the amine can be obtained by treatment with concentrated sulphuric acid. It is best purified by reduction and subsequent oxidation, and has a black colour.

mp-Ditolylamine,  $\text{C}_{14}\text{H}_{15}\text{N}$ , obtained by heating *m*-iodotoluene and *p*-toluidine with soda-lime at 335–340° for five hours, and finally for an hour at 370°, yields a hydrochloride,  $\text{C}_{14}\text{H}_{16}\text{NCl}$ , in the absence of water, and has m. p. 202–203°. The base forms a thick oil with b. p. above 300°.

nmp-Tritolylamine,  $\text{C}_{15}\text{H}_{17}\text{N}$ , obtained by heating a mixture of *m*-iodotoluene, *p*-toluidine, and soda-lime for fifteen hours at 330–330°, crystallises from alcohol in colourless needles, m. p. 89–90°, and does not combine with hydrogen chloride.

J. J. S.

Preparation of Acid Esters of Quinine Halogen Additive Products. VEREINIGTE CHININFABRIKEN ZIMMER & CO. (D.R.-P. 331961).—Ethyl hydrochloroquininecarboxylate,  $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2\text{Cl} \cdot \text{CO}_2\text{Et}$ , colourless, tasteless needles, m. p. 124°, soluble in dilute acids and reprecipitated by alkalis, is prepared by boiling a benzene solution of hydrochloroquinine with ethyl chloroformate, dissolving out the product with dilute hydrochloric acid, and reprecipitating with ammonia.

Ethyl hydrochloroisquininecarboxylate is prepared similarly, but in the presence of pyridine; it forms large, colourless, tasteless prisms, m. p. 191–192°; its solution in dilute sulphuric acid exhibits a green fluorescence.

Ethyl hydrobromoquininecarboxylate, columnar-shaped crystals, has m. p. 168–169°.

Salicylhydrobromoquinine,  $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2\text{Br} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , colourless, tasteless powder, m. p. 106–107°, is obtained by allowing quinine ethyl salicylate (1 part) dissolved in five parts of hydrobromic acid (D 1.78) to remain during a week at a temperature of 0° and then extracting the product with ether.

Benzoylhydrobromoquinine salicylate,

$\text{C}_{30}\text{H}_{28}\text{O}_4\text{N}_2\text{Br} \cdot \text{COPh} \cdot \text{C}_6\text{H}_4(\text{OH}) \cdot \text{CO}_2\text{H}$ , small leaflets, m. p. 110–115°, is prepared by leaving a solution of benzoylamine (1 part) in three parts of hydrobromic acid (D 1.78) during a night at 0°, extracting with ether, and washing with ammonium

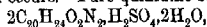
hydroxide; the ethereal solution of *benzoyl hydriobromoquinine* so obtained, is dried and treated with salicylic acid in the same solvent, when the product slowly separates.

*Ethyl hydriodoquininecarboxylate*,  $C_{20}H_{24}O_2N_2I \cdot CO_2Et$ , a pale yellow powder, m. p.  $74-78^\circ$ , is obtained by boiling together molecular proportions of hydriodoquinine and ethyl chloroformate in ethereal solution.

F. M. G. M.

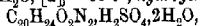
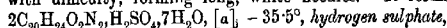
**Intramolecular Change of Quinidine (Conchicine) by Sulphuric Acid.** MICHAEL PFANNL (*Monatsh.*, 1911, 32, 241-255).

—The intramolecular changes of quinidine and of cinchonidine caused by various means have received far less attention than those of cinchonine. The present paper deals with a change of quinidine. This cannot be accomplished by the usual process of adding on a halogen acid and then eliminating it again by suitable means, because quinidine only dissolves in hydriodic acid at a temperature at which partial demethylation occurs. Pure quinidine sulphate,



$[\alpha]_D^{177.5^\circ}$  therefore, is dissolved in 66.5% sulphuric acid. After two hours at  $100^\circ$ , the specific rotation becomes constant at  $22^\circ$ . The solution is neutralised by ammonia, the liberated bases are extracted with ether, the ethereal solution is washed with water to remove the sulphonated bases (about 17% of which is formed), the ether is distilled off, and an alcoholic solution of the residue is treated with water and neutralised by hydriodic acid. By fractional crystallisation the very sparingly soluble quinidine hydriodide is easily separated from the hydriodide of the new isomeric base, which is called *isoquinidine*. A careful examination of the mother liquor shows that *isoquinidine* is the only isomeride produced.

*iso*Quinidine,  $C_{20}H_{24}O_2N_2$ , m. p.  $142^\circ$  (corr.),  $[\alpha]_D -9^\circ$ , crystallises with difficulty, forming long, white needles. It forms a *sulphate*,



$[\alpha]_D 10.2^\circ$ , *hydrogen tartrate*,  $C_{20}H_{24}O_2N_2 \cdot C_4H_6O_6 \cdot 2H_2O$ , and *hydriodide*,  $C_{20}H_{24}O_2N_2 \cdot HI$ , which is five times as soluble as quinidine hydriodide in water at  $30^\circ$ .

In the experiments, 16.5% of the quinidine is lost by sulphonation, 66% is recovered as quinidine and *isoquinidine*, and a further 13.4% in the form of the hydrogen tartrates, leaving only 4% unaccounted for.

C. S.

**Intramolecular Change of Quinidine (Conchicine) and of Cinchonidine by Sulphuric Acid.** FRITZ PANETH (*Monatsh.*, 1911, 32, 257-274. Compare preceding abstract).—The results obtained by Pfannl with quinidine are unchanged when the action of the sulphuric acid is prolonged to nine hours. With 96% sulphuric acid, however, the striking observation is made that quinidine, in the form of its hydrogen sulphate, is not converted into the isomeric *isoquinidine*, but is almost entirely sulphonated. Thus, after forty-six hours at the ordinary temperature, 15% of the quinidine is recovered unchanged,

whilst 80% has been sulphonated. At 75° the results are almost the same; 86% of the base is sulphonated, and 10% is recovered unchanged.

At the ordinary temperature, 66.5% sulphuric acid has scarcely any action on cinchonidine (in the form of the tetrasulphate), but after two hours at 100° it converts the base entirely into sulphonated products (up to 11.5%) and a new isomeride, *isocinchonidine*, m. p. 252°. (From the agreement of their other properties this base and Hesse's *iso-cinchonidine*, m. p. 235°, may be identical substances.) *isocinchonidine* has  $[\alpha]_D - 128^\circ$  in a mixture of two volumes of chloroform and one volume of 97% alcohol, and forms a *hydriodide*,  $C_{19}H_{22}ON_2HI$ , m. p. 225° (decomp.),  $[\alpha]_D - 58^\circ$  in chloroform-alcohol. Its *sulphate* in neutral solution differs from that of cinchonidine by not yielding a precipitate with potassium sodium tartrate. C. S.

**Preparation of Cotarnine Salts of Organic Acids.** MARTIN FREUND (D.R.-P. 232003).—Crystalline, well characterised derivatives of cotarnine with hydrogen sulphide, hydrogen peroxide, and hydrogen cyanide have been described (Abstr., 1900, i, 248), but the salts with organic acid have not previously been prepared.

*Cotarnine cholate*, a yellow powder, m. p. 116—120° (decomp.), is obtained by digesting cotarnine (1 mol.) with cholic acid (2, mols.) in aqueous solution, filtering, and evaporating the solution to dryness in a vacuum.

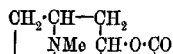
*Cotarnine phthalate*, m. p. 102°, is prepared in a similar manner with one molecular proportion of phthalic acid. F. M. G. M.

**Constitution of Dioscorine.** K. GORTER (*Rec. trav. chim.*, 1911, 30, 161—176. Compare this vol., i, 222).—Its behaviour with hydriodic acid, acetic anhydride, and potassium hydroxide proves that dioscorine does not contain methoxy- or hydroxyl groups, and that it is a  $\gamma$ -lactone. When examined by Hofmann's process of exhaustive methylation, it yields a series of products which indicate that it is a derivative of *cycloheptane*, not of *cyclohexane* as suggested previously. Thus by treatment with silver oxide, dioscorine methiodide yields a strongly alkaline hydroxide, which is converted by distillation in a vacuum into carbon dioxide, water, and a new base, *demethyldioscoridine*,  $C_{13}H_{21}N$ , b. p. 116—120°/8 mm.,  $D_4^{20}$  0.8987,  $n_D^{20}$  1.50525. The exaltation of the molecular refraction over that calculated for the formula  $C_{13}H_{21}N$  indicates that demethyldioscoridine contains a conjugated double linking. With methyl iodide, demethyldioscoridine yields a methiodide convertible by silver oxide into a hydroxide which is decomposed into trimethylamine and a *hydrocarbon*,  $C_{11}H_{14}$ , by distillation in a vacuum. Were dioscorine a derivative of *cyclohexane* this hydrocarbon would certainly be an unsaturated aromatic hydrocarbon; however, it does not yield an aromatic acid by oxidation with potassium permanganate. When a solution of the hydrocarbon in cold acetic acid is saturated with hydrogen bromide, and the yellow liquid additive compound formed is distilled with quinoline in a vacuum, a hydrocarbon is obtained which yields *o*-toluic acid by oxidation with potassium permanganate. This hydrocarbon, then,



should have the constitution  $\begin{array}{c} \text{CH}:\text{CH}\cdot\text{CMe} \\ | \\ \text{CH}:\text{CH}\cdot\text{C}\cdot\text{CH}:\text{C}_3\text{H}_5 \end{array}$ , and the original hydrocarbon would be a butenylcycloheptatriene.

Assuming this to be correct, the author advances reasons for ascribing to dioscorine the annexed constitution. This formula harmonises well with the behaviour of dioscorine and its derivatives recorded above. The presence of the group



$\text{CH}_2\text{---CH---CH---C}\cdot\text{CMe}_2$ , suggests that dioscorine should be reduced by sodium amalgam. This is so, an aqueous solution of its hydrobromide yielding *bisdihydrodioscorine*, a saturated substance,  $(\text{C}_{13}\text{H}_{20}\text{O}_2\text{N})_2$ , m. p. 266—267°, the *aurichloride* of which has m. p. 243° (decomp.).

The physiological action of dioscorine is similar to that of picrotoxin, and is connected with the presence of the group  $\cdot\text{CO}\cdot\text{C}\cdot\text{C}<$ . When the double linking is suppressed or when the lactone ring is ruptured, the resulting substances (*bisdihydrodioscorine* and *dioscoric acid* respectively) no longer have the property of causing cramp. C. S.

**Ephedrine and  $\psi$ -Ephedrine.** ERNST SCHMIDT (*Arch. Pharm.*, 1911, 249, 305—310. Compare Abstr., 1909, i, 322; Rabe, this vol., i, 396).—Dimethylephedrineammonium hydroxide, when heated in a current of steam, furnishes as nitrogen-free product an oil with an odour recalling those of dill and estragon. On treatment with trimethylamine in alcohol at 100°, this oil is, in part, converted into a substance which furnishes an *aurichloride*,  $\text{C}_9\text{H}_{10}\text{ONMe}_2\cdot\text{HAuCl}_4$ , m. p. 190—191°, which crystallises in glancing leaflets, and is sparingly soluble in water. *Dimethylephedrine aurichloride*, m. p. 185—186°, crystallises in yellow needles, and is very soluble in water. The *platinichlorides* prepared from both these substances had m. p. 249—251°, crystallised in long needles, and were sparingly soluble in water. This reaction indicates the presence in the original oil of an alkylene oxide of the formula  $\text{O} \begin{array}{l} \swarrow \text{CHPh} \\ \searrow \text{CHMe} \end{array}$ . The residue of the oil

unattacked by trimethylamine contained propiophenone and a third substance, possibly the glycol,  $\text{C}_9\text{H}_{10}(\text{OH})_2$ , which furnishes a *dibenzozate*, m. p. 83—85°, crystallising in colourless needles (compare Schmidt and Gaze, *Apoth. Zeit.*, 1911, p. 368). T. A. H.

**Sparteine. XXIII. Decomposition of *iso*Sparteine  $\alpha'$ -Methylhydroxide. XXIV. Methyl*iso*sparteine.** CHARLES MOUREU and AMAND VALEUR (*Bull. Soc. chim.*, 1911, [iv], 9, 476—478, 478—479).—These two papers give experimental details of work already published (this vol., i, 319), and add some new data.

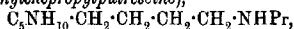
Measurements of the optical rotation of solutions of *iso*sparteine  $\alpha'$ -methyl hydroxide, to which 2 mols. of hydrogen iodide have been added, show that it does not undergo isomerisation to the  $\alpha$ -methyl hydroxide, in its formation from the  $\alpha'$ -methiodide by the action of silver hydroxide.

*Methylisosparteine*, the formation of which has been described

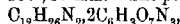
already (*loc. cit.*), has m. p.  $24^{\circ}$ , b. p.  $169-170^{\circ}/13$  mm.,  $D_4^{20}$  0.9651,  $n_D^{20}$  1.5131,  $[\alpha]_D^{20} + 23.58^{\circ}$  in alcohol. Methyl aspartate dimethiodide (*loc. cit.*), m. p.  $281-282^{\circ}$ ,  $[\alpha]_D^{20} + 21.35^{\circ}$ , is readily soluble in water or boiling methyl alcohol. T. A. H.

**The Relative Stability of the Pyrrolidine Ring.** JULIUS VON BRAUN (*Ber.*, 1911, 44, 1252—1260. Compare Abstr., 1909, i, 507, 604).—The reaction of cyanogen bromide with 1-ethylpiperidine and 1-ethylpyrrolidine proves that the pyrrolidine is less stable than the piperidine ring, for example, 34% of the ethylpiperidine compound is decomposed in such a manner that the ring is ruptured, and from 66% the ethyl group is simply removed, whereas under similar conditions practically the whole of the ethylpyrrolidine undergoes rupture. Somewhat similar results are obtained when the corresponding propyl derivatives are used. The pyrrolidine ring is thus more readily formed and also more readily ruptured than the piperidine ring, and according to Harries (*Annalen*, 1910, 374, 288), cyclopentene is more readily ruptured than cyclohexene.

1-Propylpyrrolidine,  $C_4NH_9Pr$ , obtained by the action of *n*-propylamine on *ad*-diiodobutane, is a mobile liquid with b. p.  $130^{\circ}$ . It is readily soluble in water, and has an intense basic odour. The *picrate*,  $C_{12}H_{13}O_7N_4$ , crystallises in yellow plates, m. p.  $105^{\circ}$ , and the *platinichloride*,  $C_{12}H_{25}N_2Cl_6Pt$ , forms red crystals, which begin to turn black at  $184^{\circ}$ , and are completely decomposed at  $190^{\circ}$ . The product obtained by the action of cyanogen bromide cannot be distilled, but after treatment with piperidine, it yields *pentamethylenecyanopropylputrescine*,  $C_5NH_{10}\cdot CH_2\cdot CH_2\cdot CH_2\cdot NPr\cdot CN$ , as a viscid, colourless liquid, b. p.  $191-192^{\circ}/16$  mm. Its salts are oily, and the base is comparatively stable, but when heated for twelve hours at  $155^{\circ}$  with fuming hydrochloric acid yields  *$\alpha$ -piperidino- $\delta$ -*n*-propylaminobutane* (*pentamethylenepropylputrescine*),

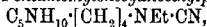


as a mobile liquid, b. p.  $130^{\circ}/10$  mm. The *picrate*,



has m. p.  $139-140^{\circ}$ , and the *platinichloride*,  $C_{12}H_{25}N_2Cl_6Pt$ , crystallises in yellow plates, m. p.  $217^{\circ}$  (decomp.).

1-Ethylpyrrolidine,  $C_6H_{13}N$ , has b. p.  $106^{\circ}$ ; the *picrate*,  $C_{12}H_{16}O_7N_4$ , crystallises in glistening plates, m. p.  $185^{\circ}$ , and the *platinichloride* does not crystallise well. *Pentamethylenecyanoethylputrescine*,



has b. p.  $182^{\circ}/16$  mm., and *pentamethylene-ethylputrescine* ( *$\alpha$ -piperidino- $\delta$ -ethylaminobutane*),  $C_6NH_{10}\cdot [CH_2]_4\cdot NHEt$ , b. p.  $125-126^{\circ}/13$  mm. The *picrate*,  $C_{11}H_{24}N_2\cdot 2C_6H_3O_7N_3$ , forms a fine yellow powder, m. p.  $113^{\circ}$ , and the *platinichloride*,  $C_{11}H_{26}N_2Cl_6Pt$ , has m. p.  $216-217^{\circ}$  (decomp.).

When tropan is treated with cyanogen bromide in ethereal solution, a small amount of methyl bromide is eliminated, but the chief product is a quaternary ammonium salt insoluble in ether. It is highly probable that this salt is formed by the rupture of the ring and the

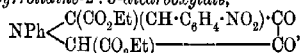
formation of a brominated cyanamide,  $CN\cdot NMe\cdot CH\begin{matrix} \nearrow CH_2\cdot CH_2\cdot CH_2 \\ \searrow CH_2\cdot CH_2\cdot CHBr \end{matrix}$

which combines with the excess of tropan, yielding the quaternary salt. The other product, *cyanonortropan*, has b. p. 148—150°/17 mm. and m. p. 108° (annexed formula), and on hydrolysis yields nortropan (Ladenburg, Abstr., 1887, 740). Cyanotropan, when heated at 150° with an excess of aniline hydrochloride and then distilled in steam, yields *s-nortropanylphenylguanidine*,  $C_{12}H_{12}N \cdot C(NH) \cdot NHPh$ , which crystallises from aqueous alcohol in glistening needles, m. p. 145°. The *picrate* has m. p. 157—158°, and the *plainichloride* decomposes at 208°. J. J. S.

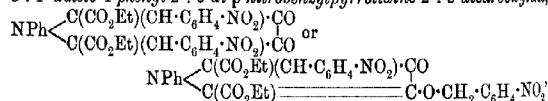
Syntheses of Pyrrole Compounds from Imino-acids. *N*-Phenyl- $\alpha\alpha'$ -dicarbethoxy- $\beta\beta'$ -diketopyrrolidine [Ethyl 3:4 Diketo-1-phenylpyrrolidine-2:5-dicarboxylate]. TREAT B. JOHNSON and ROBERT BENGIS (*J. Amer. Chem. Soc.*, 1911, 33, 745—755). —It has been shown by Johnson and Johns (Abstr., 1906, i, 874) that ethyl oxalate condenses with ethyl diglycollate with formation of ethyl 3:4-diketotetrahydrofuran-2:5-dicarboxylate. In continuation of this work, a study has now been made of the condensation of ethyl oxalate with ethyl phenylglycinoacetate.

Mouilpied (Trans., 1905, 87, 435) has found that ethyl oxalate condenses with ethyl phenylglycinoacetate in presence of sodium ethoxide to form a compound,  $C_{16}H_{17}O_6N$ , m. p. 137°, to which he was unable to assign a satisfactory constitutional formula, but regarded it as having a quinonoid structure, as it yields a yellow sodium salt. A re-investigation of this substance has shown that it is ethyl 3:4-diketo-1-phenylpyrrolidine-2:5-dicarboxylate,  $NPh \begin{matrix} \text{CH}(\text{CO}_2\text{Et}) \cdot \text{CO} \\ \text{CH}(\text{CO}_2\text{Et}) \cdot \text{CO} \end{matrix}$ . This compound gives a yellow di-sodium salt and a colourless *mono-sodium* salt; the *barium* salt crystallises with  $1H_2O$ .

When the yellow sodium salt is heated with *p*-nitrobenzyl chloride in presence of alcohol, a small quantity of ethyl 3:4-diketo-1-phenyl-2-*p*-nitrobenzylpyrrolidine-2:5-dicarboxylate,



m. p. 180—182° (decomp.), is obtained as an orange-coloured powder. The main product of the reaction, however, is ethyl 3:4-diketo-1-phenyl-2:5-di-*p*-nitrobenzylpyrrolidine-2:5-dicarboxylate,



m. p. 132°, which forms yellow prisms.

Attempts to reduce ethyl 3:4-diketo-1-phenylpyrrolidine-2:5-dicarboxylate with hydriodic acid and also with aluminium amalgam were not successful.

Mouilpied (*loc. cit.*) observed that if the condensation of ethyl oxalate with ethyl phenylglycinoacetate is effected in presence of sodium methoxide instead of the ethoxide, the ethyl ester, m. p. 137°, is not produced, but the corresponding methyl ester, m. p. 188°, is

formed. He therefore carried out the several condensations of methyl and ethyl oxalates with methyl and ethyl phenylglycinoacetates in presence of sodium methoxide and of sodium ethoxide. From these eight condensations, he obtained six different compounds. These experiments have now been repeated, and it has been found that only two compounds are actually produced. The compound, m. p.  $137^{\circ}$ , is formed by the condensation of ethyl or methyl oxalate with ethyl or methyl phenylglycinoacetate in presence of sodium ethoxide, whilst by the condensation of these esters in presence of sodium methoxide, the compound, m. p.  $188-189^{\circ}$ , is obtained. It is evident, therefore, that the product of the reaction is determined by the particular alkyl oxide used. The compound, m. p.  $188-189^{\circ}$ , is methyl 3:4-diketo-1-phenylpyrrolidine-2:5-dicarboxylate. E. G.

**Pyridinoiridopentachlorides.** MARCEL DELÉPINE (*Compt. rend.*, 1911, 152, 1390—1393. Compare Abstr., 1908, ii, 702; 1910, ii, 44).—The metallic pyridinoiridopentachlorides are formed by introducing a molecule of pyridine into an aquoiridopentachloride in place of  $1\text{H}_2\text{O}$ , or into an alkali iridohexachloride in place of a molecule of alkali chloride.

*Potassium, sodium, and ammonium pyridinoiridopentachlorides* conform to the type  $\text{IrCl}_5(\text{C}_5\text{H}_5\text{N})\text{M}_2$ , and are best prepared by treating a hot solution of the iridochloride with excess of pyridine and removing the excess as rapidly as possible. The products vary in colour from orange to red according to the size of the crystals. The *thallium, silver, mercurous, and mercuric* salts are amorphous and insoluble in water. Orange crystals having the composition  $\text{IrCl}_5(\text{C}_5\text{H}_5\text{N})(\text{NH}_4\text{Ag})_2\cdot\text{H}_2\text{O}$  are obtained when the silver salt is dissolved in ammonia. The alkali salts are very stable, and the pyridine is not removed by concentrated sulphuric acid at  $100^{\circ}$ . Chromic acid and hydrogen peroxide are without action, but chlorine and nitric acid convert them into a new series of salts of the type  $\text{IrCl}_6(\text{C}_5\text{H}_5\text{N})\text{M}$ . W. O. W.

**Pyridinoiridipentachlorides.** MARCEL DELÉPINE (*Compt. rend.*, 1911, 152, 1589—1591. Compare preceding abstract).—The pyridinoiridipentachlorides of the type  $\text{IrCl}_5(\text{C}_5\text{H}_5\text{N})\text{M}$  are related to the pyridinoiridopentachlorides previously described, in the same way as the iridihexachlorides are to the iridohexachlorides. They are best obtained by the action of nitric acid on the corresponding pyridinoiridopentachlorides. The *potassium, ammonium, rubidium, caesium, and sodium* salts form very deep red crystals, and are anhydrous except in the last case. Like the pyridinoiridopentachlorides they give precipitates with aqueous solutions of thallium, silver, mercurous, and mercuric salts, but differ from them in giving no precipitate with lead salts. The *silver* salt crystallises in slender, violet needles.

These salts are remarkably stable towards acids, but lose pyridine when heated with hydrochloric acid in sealed tubes at  $150-160^{\circ}$ , giving the corresponding hexachlorides. W. O. W.

**Pyridylacetylcatechol and Related Bases.** CARL MANNICH and O. HÜNNER (*Ber. Deut. pharm. Ges.*, 1911, 21, 294—297. Compare Abstr., 1910, i, 411).—A number of bases somewhat similar in structure to

adrenaline have been prepared by condensing pyridine, piperidine, or quinoline with chloroacetyl catechol or the bromoacetyl derivative of catechol dimethyl ether.

Chloroacetyl catechol,  $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{CO} \cdot \text{CH}_2\text{Cl}$ , condenses with pyridine when gently warmed with it in alcohol to form *pyridylacetyl catechol hydrochloride*,  $\text{C}_6\text{H}_3(\text{HO})_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{C}_5\text{NH}_3\text{Cl}$ , m. p.  $272^\circ$  (decomp.), which crystallises from hot water, and on addition of ammonia yields the free base (or pseudo-base), m. p.  $199^\circ$  (decomp.), in the form of yellow crystals. *Pyridylacetyl veratrole hydrobromide*,

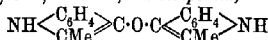
$\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{C}_5\text{NH}_3\text{Br}$ , m. p.  $258^\circ$  (decomp.), similarly obtained, also crystallises from hot water, but the free base could not be isolated by the action of alkalis. When heated with hydrochloric acid, the methoxyl groups were eliminated and pyridylacetyl catechol hydrochloride was formed.

*Piperidylacetyl catechol hydrochloride*, m. p.  $257^\circ$  (decomp.), forms colourless needles from water; the free base, m. p.  $199-205^\circ$  (decomp.), is liberated from the hydrochloride by ammonia. *Quinolylacetyl veratrole hydrobromide*,  $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{C}_9\text{NH}_3\text{Br}$ , m. p.  $222^\circ$  (decomp.), crystallises from hot water. With ammonia it furnishes a reddish-brown, amorphous product, and when heated with hydrochloric acid yields a product,  $\text{C}_{17}\text{H}_{14}\text{O}_3\text{NCl}$ , m. p.  $248^\circ$  (decomp.), which separates from water in yellowish-brown crystals and gives catechol reactions. The free base could not be obtained. Quinoline does not condense directly with chloroacetyl catechol.

T. A. H.

**New Oxidation of 2-Methylindole.** GIUSEPPE PLANCHER and U. COLACICCHI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 453-457).—With the exception of fusion with potassium hydroxide, all methods previously used for the oxidation of 2-methylindole result in the rupture of the nucleus and the formation of anthranilic acid and its substitution products.

Oxidation of 2-methylindole by means of 15% ethereal hydrogen peroxide solution yields, however, the compound,



or  $\text{CH} \begin{array}{c} \text{CMe} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{N} \cdot \text{O} \cdot \text{N} \begin{array}{c} \text{CMe} \\ \diagdown \quad \diagup \\ \text{C}_6\text{H}_4 \end{array} \text{CH}$ , which forms greenish-yellow crystals, m. p.  $209-210^\circ$ , and has the normal molecular weight in freezing naphthalene. It gives a red coloration with boiling acetic acid, whilst with concentrated sulphuric acid it yields a blue solution, which becomes green and deposits green flocks on dilution with water. On reduction with tin and hydrochloric acid, it gives dihydro-2-methylindole.

The same product is formed from 2-methylindole by oxidation with aqueous hydrogen peroxide or Caro's acid, and together with other compounds, not yet studied, with ozone in presence of water or chloroform.

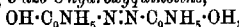
Attempts to oxidise 2-phenylindole and 2:3-dimethylindole by means of hydrogen peroxide have as yet led to no definite results.

T. H. P.

8-Hydroxyquinoline. GEORG COHN (*J. pr. Chem.*, 1911, [ii], 83, 498—506).—8-Hydroxyquinoline and formaldehyde, which yield hydroxymethyl-8-hydroxyquinoline under Manassé's conditions (*Abstr.* 1903, i, 28), produce another substance, called "*new hydroxyquinoline-carbinol*," when a mixture of 5 grams of 8-hydroxyquinoline, 15 c.c. of formalin, and 10 c.c. of 20% sodium hydroxide are heated on the water-bath; by dilution with water and neutralising with hydrochloric or acetic acid, the new compound,  $C_{12}H_9O_3N$ , is obtained as a yellow, amorphous powder. It does not melt at  $250^\circ$ , evolves formaldehyde at higher temperatures, forms a solution in dilute hydrochloric acid which is coloured dark green by ferric chloride, yields a yellow sodium salt, couples with diazobenzenesulphonic acid, and is oxidised by alkaline potassium ferricyanide to a dark green substance.

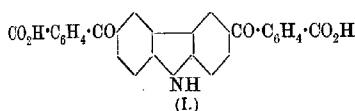
8-Hydroxyquinoline-5-sulphonic acid is formed when loretin (7-iodo-8-hydroxyquinoline-5-sulphonic acid) is boiled with water and aniline or phenetidine, with piperidine, or with guaiacol and sodium hydroxide.

5-Nitroso-8-hydroxyquinoline is reduced by phenylhydrazine on the water-bath, yielding 5-azo-8-hydroxyquinoline,

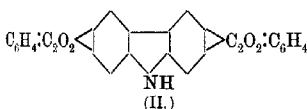


m. p.  $220^\circ$  (decomp.), brownish-red needles with a blue reflex. By reduction with potassium sulphite the nitroso-compound yields a substance, not yet fully examined, which is probably an amino-hydroxyquinolinesulphonic acid. C. S.

Introduction of Several Phthalic Acid Groups into Aromatic Compounds. IV. Experiments with Carbazole. ROLAND SCHOLL and WERNER NEOVIUS (*Ber.*, 1911, 44, 1249—1252.



without a diluent, yielding carbazole-3:6-diphthaloylic acid (I.), and



Compare this vol., i, 452, 453, 557).—Carbazole reacts with phthalic anhydride and aluminium chloride, either with or without a diluent, yielding carbazole-3:6-diphthaloylic acid (I.), and this reacts with concentrated sulphuric acid at  $90^\circ$  and then at  $100^\circ$ , yielding 2:3:6:7-diphthaloyl-carbazole (II.). In the preparation of the dibasic acid

a certain amount of the *N*-phthaloylic acid (carbazole-*N*-carbonyl-*o*-benzoic acid: Stummer, *Abstr.*, 1907, i, 723) is formed, and can be removed by hydrolysis with sodium hydroxide, and also a certain amount of the 3-phthaloylic acid, which is removed by adding a small amount of magnesium sulphate to the solution of the ammonium salts. The dibasic acid,  $C_{28}H_{17}O_6N$ , forms a colourless, amorphous powder, m. p.  $300-301^\circ$ .

2:3:6:7-Diphthaloylcarbazole,  $C_{28}H_{15}O_4N$  (II.), crystallises from quinoline in golden-yellow needles, which are not molten at  $450^\circ$ . With alkaline hyposulphite solutions, it yields a dark brown vat-dye.

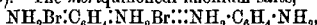
J. J. S.

**Oximes and Phenylalkylisooxazolones Obtained from Ethyl Benzoylpropionate, Benzoyl-*n*-butyrate, and Benzoylisobutyrate.** ALBIN HALLER and EDMOND BAUER (*Compt. rend.*, 1911, 152, 1446—1450. Compare this vol., i, 299).—The substance, m. p. 91°, obtained by Hantzsch and Miolati (*Abstr.*, 1893, 583) by acting on ethyl benzoyl-*n*-butyrate with hydroxylamine hydrochloride and potassium hydroxide gives analytical results indicating it to be *phenylethylisooxazolone*, and not an oxime, as these authors supposed. The corresponding *oxime*, however, is formed when the ester is treated with hydroxylamine zincchloride in alcoholic solution, and occurs in prisms, m. p. 80—81°. Similar results were obtained with alkyl derivatives of ethyl benzoylacetate, Crismer's reagent always leading to the production of an oxime, and hydroxylamine to that of a phenylisooxazolone. The latter is also formed by withdrawing  $\text{H}_2\text{O}$  from the oxime.

*Phenylmethylisooxazolone*,  $\text{C}_{10}\text{H}_9\text{O}_2\text{N}$ , has m. p. 123—124°; *phenyl-dimethylisooxazolone*,  $\text{CMe}_2\text{C}(\text{OPh})=\text{N}$ , has m. p. 70—71°.

W. O. W.

**The Simplest Quinonoid Dyes.** JEAN PICCARD (*Annalen*, 1911, 381, 351—366).—The *meriquinonedi-imonium* salts,

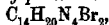


and their methyl derivatives exist in  $\alpha$ - and  $\beta$ -modifications (compare *Abstr.*, 1910, i, 66). The  $\alpha$ -compounds exhibit characteristic absorption spectra, all of much the same type, although the colour of the solutions passes from yellow through orange, red, and violet to blue with an increase in the number of methyl groups present. The more strongly coloured salts, the  $\beta$ -modifications, are most readily obtained at low temperatures, especially in the presence of water, whereas alcohol favours the formation of the  $\alpha$ -compounds. The solutions, as a rule, consist of equilibrated mixtures, but the equilibrium can be appreciably altered by changing the conditions. The imonium salt itself and its mono- and di-methyl derivatives exist in the solid state as the  $\beta$ -forms only, whereas the tri- and tetra-methyl derivatives exist as the solid  $\alpha$ -forms. The absorption spectra of the  $\beta$ -modifications are essentially different from those of the  $\alpha$ , and do not consist of a number of characteristic bands. By the use of the colorimetric dilution law (this vol., ii, 561,) it is shown that the  $\alpha$ - and  $\beta$ -modifications are not isomeric, but polymeric, and the conversion of the  $\beta$ - into the  $\alpha$ -form consists in depolymerisation or dissociation.

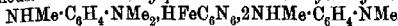
The rate of transformation is extremely rapid, so that a given salt does not exist in both forms under given specific conditions. The  $\alpha$ -form of the *meriquinonedi-imonium* bromide exists only in dilute solution at 0°; under all other conditions the  $\beta$ -form is the stable form, but with the tetramethyl derivative the  $\alpha$ -form is the only one which has been observed either in the solid state or in solution.

As a rule, the  $\beta$ - are more stable than the  $\alpha$ -compounds. *meri-Quinonedi-imonium* bromide (compare Jackson and Calhane, *Abstr.*, 1902, i, 645; Pringsheim, *ibid.*, 1905, i, 934; Kehrman, *ibid.*, 1906, i, 46) crystallises as a heavy, brown powder with a golden-yellow

lustre when it is deposited gradually from a mixture of alcohol and glacial acetic acid. The corresponding nitrate,  $C_{12}H_{10}O_6N_6$ , has a brassy lustre. The merimethylquinonedimmonium bromide,



is amorphous. meriTrimethylquinonedimmonium ferricyanide,



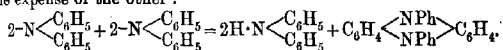
crystallises in brilliant black needles.

J. J. S.

**Aromatic Hydrazines. IX. Tetraphenylhydrazine and Hexaphenylethane.** HEINRICH WIELAND (*Annalen*, 1911, 381, 200—216).—Tetra-arylated hydrazines are readily hydrolysed to diarylated amines and diarylated hydroxylamines, but as the latter are unstable they cannot be directly isolated, but are transformed into decomposition or condensation products (compare Abstr., 1906, i, 830; 1907, i, 1076; 1908, i, 1014, 1026; this vol., i, 83).

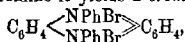
It is now shown that tetraphenylhydrazine is partly depolymerised (dissociated) when boiled with toluene, and thus resembles hexaphenylethane, which is partly dissociated into triphenylmethyl in benzene solution. It has not been found possible to isolate the primary dissociation product,  $-NPh_2$ , as this is extremely unstable and undergoes further transformation.

[With HANS LECHER.]—When the toluene solution of tetraphenylhydrazine is boiled, a green colour is developed, but this changes rapidly to brown, and on cooling the colour does not disappear. After boiling for thirty minutes, removing the toluene under reduced pressure, and then adding ether, crystals of diphenyldihydrophenazine are obtained, and diphenylamine and *o*-anilinetriphenylamine remain in solution. Details for the separation of the three compounds are given. The diphenylamine and diphenyldihydrophenazine are regarded as being formed by the reduction of one portion of the dissociation product at the expense of the other:



This reaction is analogous to the formation of triphenylmethane and a complex bimolecular hydrocarbon from triphenylmethyl. The formation of *o*-anilinetriphenylamine [triphenyl-*o*-phenylenediamine],  $NHPh \cdot C_6H_4 \cdot NPh_2$ , from tetraphenylhydrazine is due to a semidine transformation, and is analogous to the formation of benzhydryltetraphenylmethane from hexaphenylethane, except that in the latter case the substituents occupy the para-position.

Diphenyldihydrophenazine,  $C_{24}H_{18}N_2$ , crystallises from a mixture of benzene and alcohol in colourless needles, m. p. 172—175°. On exposure to the air it turns green, as it is readily oxidised to a quinonoid salt. Its benzene solutions have more or less colloidal properties, and with bromine it yields a bromide,



the chloroform solutions of which have a brilliant green colour.

Triphenyl-*o*-phenylenediamine,  $C_{24}H_{20}N_2$ , is amorphous, has m. p. 85°, and yields a crystalline hydrochloride. The base reacts with bromine, evolving hydrogen bromide and yielding diphenyldihydrophenazine



dibromide. The blue compound obtained by treating diphenylamine with concentrated sulphuric acid and an oxidising agent is shown to be identical with the *o*-quinonoid sulphate of diphenyldihydrophenazine,  $C_6H_4 \begin{smallmatrix} \text{NPh}(\text{O}\cdot\text{SO}_3\text{H}) \\ \text{NPh}(\text{O}\cdot\text{SO}_3\text{H}) \end{smallmatrix} > C_6H_4$ , and its formation is due to the following series of reactions. Oxidation of diphenylamine to tetraphenylhydrazine, hydrolysis of the latter to diphenylamine and diphenylhydroxylamine, and condensation of the hydroxylamine to diphenyldihydrophenazine (phenoperazine), and, finally, oxidation of this to the *o*-quinonoid salt.

The dissociation of tetraphenylhydrazine can also be shown by passing nitric oxide into a toluene solution of the hydrazine, heated at 90–95° and protected from atmospheric oxygen. After some twenty to thirty minutes the hydrazine is transformed quantitatively into diphenylnitrosoamine. The nitrosoamine when heated at 130° gives a theoretical yield of nitric oxide, showing that the reaction is reversible. The other products are diphenylamine and diphenyldihydrophenazine, although the amount of the latter is very small. Di-*p*-tolynitrosoamine and di-*p*-anisylnitrosoamine behave in a similar manner. Nitrosocarylamides behave in quite a different manner



(Bamberger, Abstr., 1894, i, 412; 1910, i, 908); when heated in an indifferent solvent, for example, light petroleum, they explode or evolve nitrogen, but not nitric oxide. The annexed structural formula is suggested for these compounds.

When triphenylmethyl is heated on the water-bath with a toluene solution of tetraphenylhydrazine in the absence of air, crystals of *triphenylmethyldiphenylamine*,  $CPh_3\cdot NPh_2$ , are obtained. The formation of this compound is due to the union of the two unsaturated groups,  $CPh_3$ - and  $-NPh_2$ . It forms large, colourless, transparent needles, m. p. 172°, and with concentrated sulphuric acid yields triphenylcarbinol and diphenylamine. In boiling xylene the compound is partly dissociated the solution has a red colour, and gives all the characteristic reactions of triphenylmethyl. *Triphenylmethyldi-p*-tolylamine,  $C_{35}H_{35}N$ , has m. p. 164°, and, like the diphenylamine derivative, gives a red melt.

Tetraphenyl-, di-*p*-tolyl-, and di-*p*-anisyl- hydrazines give a blue phosphorescence when subjected to the action of cathode rays, and themselves turn green in the course of a few seconds. Tetratolylhydrazine and *p*-tetradiphenylhydrazine are coloured dark yellow, but these colours disappear rapidly when the substances are removed from the influence of the cathode rays.

J. J. S.

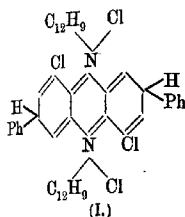
**Aromatic Hydrazines. X. Tetradiphenylhydrazine.** HEINRICH WIELAND and ARTHUR SÜSSER (*Annalen*, 1910, 381, 217–229. Compare preceding abstract).—Tetradiphenylhydrazine is not dissociated so readily as tetraphenylhydrazine, and its properties resemble tetra-*p*-tolyl- rather than tetraphenylhydrazine. It is prepared by oxidising an acetone solution of *p*-didiphenylamine with finely-powdered permanganate at 10°. *p*-Didiphenylamine,  $NH(C_{12}H_9)_2$ , can be obtained as its acetyl derivative by boiling *p*-iododiphenyl and *p*-acetylaminodiphenyl, potassium carbonate, copper bronze, a

little iodine, and potassium iodide with nitrobenzene for twenty-four hours. The base, obtained by hydrolysing the acetyl derivative with alcoholic potassium hydroxide, crystallises from benzene or xylene in glistening, nacreous plates, m. p. 209°. The *hydrochloride* forms long prisms; the *nitrosoamine*,  $C_{24}H_{18}ON_2$ , crystallises from benzene in yellow needles, m. p. 172°.

*Tetradiphenylhydrazine*,  $N_2(C_6H_5Ph)_4$ , crystallises slowly from a mixture of benzene and alcohol, has m. p. 165°, and, when warmed with glacial acetic acid, gives a characteristic intense violet coloration. When boiled for some time in xylene solution, dissociation can be recognised by the separation of the sparingly soluble didiphenylamine.

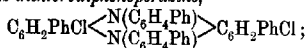
*Didiphenyldihydrophenazine*,  $C_{48}H_{34}N_2$ , does not appear to be formed, but was met with in the mother liquors from the

hydrazine after they had been kept for several months. It crystallises from xylene in yellow needles, m. p. 325–330°, and yields a *hydrochloride* in the form of broad, violet needles, with a quinonoid constitution.



The hydrazine combines with hydrogen chloride in the presence of benzene, light petroleum, and ether, yielding a flocculent, green *hydrochloride*,  $C_{48}H_{38}N_2 \cdot 2HCl$ , which is gradually transformed into didiphenylamine hydrochloride, the violet

*chloride of dichlorodiphenoperazine*, together with an isomeride of the tetra-arylated hydrazine and *o*-chlorodiphenylamine. The violet chloride (I), when treated with a little ammonia or alcoholic potassium hydroxide, yields *dichlorodiphenoperazine*,



this crystallises from xylene in yellow needles, which are not molten at 380°. When reduced with sodium and amyl alcohol in the presence of xylene the dichloro-derivative yields didiphenyldihydrophenazine (diphenoperazine). The isomeride of the hydrazine is probably *o*-diphenylaminotridiphenylamine,  $C_6H_4Ph \cdot NH \cdot C_6H_3Ph \cdot N(C_6H_4Ph)_2$ ; it crystallises from hot xylene in felted needles, m. p. 275°, and gives a green coloration with ferric chloride or with bromine.

*o*-Chlorodidiphenylamine,  $C_{24}H_{18}NCl$ , crystallises from alcohol, melts to a turbid liquid at 119°, and becomes clear at 130°.

Tetradiphenylhydrazine and bromine yield an unstable, dark green bromide, which is rapidly decomposed, yielding didiphenylamine and *dit bromodidiphenylamine*,  $C_{24}H_{17}NBr_2$ , in the form of long, glistening needles, m. p. 151°.

J. J. S.

**The Stability of the Nitrogen Linking in Ketazines.**  
HEINRICH WIELAND and A. ROSSEU (*Annalen*, 1911, 381, 229–233).—According to Curtius and his pupils, the ketazines which contain a grouping similar to nitric oxide (bimolecular form),  $O:N:N:O$  and  $R_2C:N:N:CR_2$ , are extremely stable and do not dissociate. The ketazines derived from the following ketones have been prepared and

examined: benzophenone, fluorenone, and tetramethyldiamino-benzophenone. All the compounds are stable, they dissolve in concentrated sulphuric acid without decomposition, can be distilled to a certain extent without decomposition, and when hydrolysed by hot mineral acids yield hydrazine and ketone.

Benzophenoneketazine (Curtius and Rauterberg, *J. pr. Chem.*, 1901, 63, 94) is quite colourless, but its solutions have a yellow colour, and the intensity of the colour in different solvents increases in the order: Ethyl alcohol, ether, acetone, benzene, chloroform. It yields an unstable lemon-yellow hydrochloride and a reddish-orange bromide.

*Fluorenonehydrazone*,  $\begin{matrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{matrix} > \text{C}:\text{N}\cdot\text{NH}_2$ , is formed when the ketone and hydrazine hydrate are warmed with a little alcohol on the water-bath, and crystallises from alcohol in pale yellow plates, m. p. 149°. When oxidised with the theoretical amount of iodine in alcoholic solution, it yields *fluorenoneketazine*,  $\begin{matrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{matrix} > \text{C}:\text{N}\cdot\text{N}\cdot\text{C} < \begin{matrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{matrix}$ , and nitrogen. The ketazine crystallises from xylene in brilliant dark red needles, m. p. 259°, and its solution in concentrated sulphuric acid has a purple-red colour. When reduced with zinc dust and glacial acetic acid it yields 9-aminofluorene.

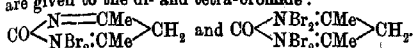
*Tetramethyl-p-diaminodiphenylketone hydrazone*,  $\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{N}\cdot\text{NH}_2$ , obtained by heating the components with a little alcohol at 180°, crystallises from alcohol in pale yellow needles, m. p. 150°. The *benzylidene* derivative,  $\text{C}_{24}\text{H}_{20}\text{N}_4$ , crystallises from alcohol in pale orange-yellow needles, m. p. 141°, and the *ketazine*,  $\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{N}\cdot\text{N}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ , obtained by oxidising the hydrazone with mercuric oxide and a little iodine, crystallises from xylene in large, brownish-red prisms, m. p. 253°. Its solution in concentrated sulphuric acid is practically colourless.

J. J. S.

**Preparation of 5:5-dialkyliminobarbituric Acid (2-Imino-4:6-diketo-5:5-dialkylpyrimidine).** EMANUEL MERCK (D.R.P. 231887).—When 5:5-dialkylmalonic acid diaryl esters are heated with guanidine (or a guanidine salt), they yield imino-5:5-dialkylbarbituric acids. 2-Iminodiethylbarbituric acid, prepared by heating diphenyl diethylmalonate with guanidine carbonate at 160°, may subsequently be converted into diethylbarbituric acid. F. M. G. M.

**Relationships between Perbromides and Bromo-substitution Products Observed with Acetylacetonecarbamide [4:6-Dimethyl-2-pyrimidone] and its Tautomeride.** ORTO STARK (*Annalen*, 1911, 381, 143—199).—Evans's acetylacetonecarbamide [4:6-dimethyl-2-pyrimidone] (Abstr., 1893, i, 129; 1894, i, 111; Stark, 1909, i, 259) combines with two or with four atoms of bromine, yielding products which are regarded as perbromides and not as compounds formed by the addition of bromine to unsaturated linkings, since the bromine is not firmly attached to the molecule. As pyridine and quinoline also yield perbromides, it is suggested that the bromine

combines with the nitrogen atoms of the molecule, and the following formulae are given to the di- and tetra-bromide:



To distinguish the two tautomeric forms, the name acetylacetone-carbamide will be used in this abstract for the original compound and 4:6-dimethyl-2-pyrimidone for its isomeride. The latter also yields perbromides, and these with water or alcohol yield the same products as are obtained from the perbromide of the carbamide. The two sets of perbromides are not regarded as being identical, since the one from the pyrimidone loses its colour more rapidly than that derived from the carbamide.

The perbromide of acetylacetonecarbamide,  $\text{C}_6\text{H}_8\text{ON}_2\text{Br}_2$ , can be obtained by the addition of bromine to a chloroform solution of the carbamide (Abstr., 1909, i, 259), or to a solution of the carbamide in hydrobromic acid (b. p. 121°). In the latter case orange-yellow needles are obtained, which darken in colour when heated, but have no definite m. p. When triturated with water, it yields a pentabromide,  $\text{C}_6\text{H}_8\text{ON}_2\text{Br}_5$ , Evans's dibromodihydroxy-derivative (5-dibromo-4:6-dihydroxy-4:6-dimethyl-2-tetrahydropyrimidone), and 5-bromo-4:6-dimethyl-2-pyrimidone.

The last compound is contained in the aqueous liquid, and can be isolated as its sodium derivative. The first two compounds are present in the colourless solid, and after this has been dried the pentabromo-derivative can be extracted by chloroform.

5-Dibromo-4:6-dihydroxy-4:6-dimethyl-2-tetrahydropyrimidone,  $\text{CO} \begin{array}{c} \text{NH}\cdot\text{CMe}(\text{OH}) \\ \text{NH}\cdot\text{CMe}(\text{OH}) \end{array} \text{CBr}_2$ , is sparingly soluble in most solvents; its solubility in ethyl alcohol is 1 in 100, but at the same time it undergoes partial decomposition, yielding a dye, which crystallises in deep violet prisms.

The same decomposition occurs when the compound is boiled or kept some time in contact with water, and also when the solid is heated for some time at 100°. With carbon disulphide, the dihydroxy-derivative forms a gelatinous mass, which crystallises on the addition of a solvent miscible with carbon disulphide. It dissolves in cold sodium hydroxide solution (4 mols.), and when acidified after two to three hours yields carbon dioxide, acetic and lactic acids, ammonia, and hydrobromic acid. It is claimed that the formation of these products is more in harmony with the author's view of the constitution of the dihydroxy-derivative than with Evans's view.

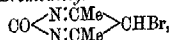
Colourless anhydrous 4:6-dimethyl-2-pyrimidone is obtained when anhydrous acetylacetonecarbamide is dissolved in absolute alcohol, mixed with the theoretical amount of sodium ethoxide, the precipitated sodium derivative removed, dried, suspended in absolute alcohol, and dry carbon dioxide passed in. The filtered solution is evaporated to dryness at the ordinary temperature over potassium hydroxide and concentrated sulphuric acid, and the residue crystallised from acetone, when the pyrimidone is obtained as colourless, glistening needles, m. p. 200°.

Acetylacetonecarbamide perbromide,  $\text{C}_6\text{H}_8\text{ON}_2\text{Br}_4$ , obtained from

either chloroform or distilled hydrobromic acid solution, forms red, microscopic needles; it has no definite m. p., it changes colour at 150° to 160°, and is completely decomposed at 220°. With water it yields 5-dibromo-4:6-dihydroxy-4:6-dimethyl-2-tetrahydropyrimidone and 5-bromo-4:6-dimethyl-2-pyrimidone.

By the action of a solution of bromine in dilute acetic acid on a glacial acetic acid solution of acetylacetonecarbamide at 30–40° it has not been found possible to obtain the bromohydroxy-derivative previously described (*loc. cit.*); the only product obtained was the *hydrobromide* of the carbamide,  $C_8H_8ON_2 \cdot HBr$ . The same product was also obtained by the action of alcohol on the perbromide of the carbamide, and by dissolving the carbamide in a mixture of glacial acetic acid and concentrated hydrobromic acid. It crystallises from alcohol in colourless needles, which decompose at 345° after changing colour at 240–250°.

An aqueous solution of sodium hypobromite reacts with acetylacetonecarbamide, yielding the *sodium* salt of 5-bromo-4:6-dimethyl-2-pyrimidone, in the form of slender, colourless needles, decomposing rapidly at 336–338°. The corresponding hydrogen compound exists in two forms. *Bromoacetylacetonecarbamide*,



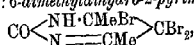
obtained by the action of acetic acid on the sodium salt, crystallises in pale yellow needles or prisms, and decomposes at 228–231°.

5-Bromo-4:6-dimethyl-2-pyrimidone,  $CO \begin{array}{c} \text{NH} \cdot CMe \\ \text{N} = CMe \end{array} > CBr$ , obtained

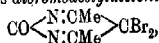
by boiling the sodium salt and the theoretical amount of acetic acid, crystallises in colourless needles or in colourless, glistening prisms. The yellow compound can be transformed into the colourless by boiling with water and adding a few drops of concentrated ammonium hydroxide solution, and can be transferred back into the yellow modification by boiling with dilute acetic acid. The monobromo-derivative yields a colourless *nitrate*,  $C_8H_8ON_2Br \cdot HNO_3$ , in the form of glistening needles, which decompose between 160° and 200°; it also yields a reddish-yellow *dinitrate*,  $C_8H_8ON_2Br \cdot 2HNO_3 \cdot 3H_2O$ , which explodes at about 196–197°.

The *perbromide* of bromoacetylacetonecarbamide,  $C_8H_8ON_2Br_2$ , forms chrome-yellow needles, decomposes at 160–200°, and with water yields 5-dibromo-4:6-dihydroxy-4:6-dimethyltetrahydro-2-pyrimidone. The bromopyrimidone also yields a perbromide with  $Br_2$ , but this rapidly becomes colourless when kept.

5:5:6-Tribromo-4:6-dimethyldihydro-2-pyrimidone,



obtained by mixing a chloroform solution of 5-bromo-4:6-dimethyl-2-pyrimidone with a chloroform solution of bromine at 30–40°, and shaking at the given temperature until hydrogen bromide is evolved, forms colourless crystals, which begin to decompose at 220–240°. It cannot be recrystallised, and when heated with chloroform or treated with water yields *dibromoacetylacetonecarbamide*,



as colourless needles, decomposing at 160—170°. When water is used, *bromoacetylacetonecarbamide hydrobromide*,  $C_6H_5ON_2Br_2$ , is also formed. This crystallises from methyl alcohol. The *perbromide* of the monobromo-derivative,  $C_6H_5ON_2Br_4$ , forms red needles, decomposing between 160° and 200°.

[With P. HOBMANN.]—When acetylacetonecarbamide or its monobromo-derivative is brominated in the presence of boiling chloroform, hydrogen bromide is evolved during ten to twelve hours, and the following products are formed: (1) The pentabromide (see above), which remains dissolved in the chloroform; (2) a heptabromide which is insoluble in chloroform, but soluble in benzene; (3) perbromides, insoluble in chloroform and benzene; these on treatment with water yield the dibromodihydroxydimethylidihydropyrimidone and the hydrobromide of bromoacetylacetonecarbamide. The *pentabromide*, probably  $CO \begin{smallmatrix} \text{NH} \cdot \text{CBr}(\text{CH}_2\text{Br}) \\ \text{NH} \cdot \text{CBr}(\text{CH}_2\text{Br}) \end{smallmatrix} > \text{CHBr}$ , is stable, and crystallises from chloroform or benzene in well-developed, pale yellow prisms, m. p. 183—184° (decomp.). It is not appreciably decomposed when boiled with water for two to three hours, is distinctly acidic, and yields a sodium salt,  $C_6H_5ON_2Br_5Na$ , in the form of slender, colourless needles, which are not decomposed by carbonic acid. It also yields a *hydrobromide* in the form of a yellow, crystalline precipitate, which decomposes when removed from the mother liquor. The *heptabromide*,  $C_6H_5ON_2Br_7$ , crystallises from benzene with partial decomposition in yellow, felted needles, and also tends to give up bromine when kept in a desiccator. It is most readily prepared by the addition of bromine to the pentabromide, and yields the pentabromide by the action of hydroxylic compounds.

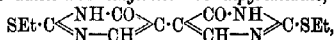
A table showing the genetic relationships of the different bromo-derivatives is given. J. J. S.

#### Pyrimidines. LI. Synthesis of Cytosine-5-acetic Acid.

TREAT B. JOHNSON [with HARLEY T. PECK and JOSEPH A. AMBLER] (*J. Amer. Chem. Soc.*, 1911, 33, 758—766).—It has been shown by Johnson and Speh (Abstr., 1907, i, 1083) that  $\psi$ -ethylthiocarbamide condenses with the sodium derivative of ethyl formylsuccinate to form ethyl 2-ethylthiol-6-pyrimidone-5-acetate. When this compound is heated with phosphoryl chloride, *ethyl 6-chloro-2-ethylthiolpyrimidine-5-acetate*,  $N \begin{smallmatrix} \text{C}(\text{SEt}) \\ \text{CCl} \cdot \text{C}(\text{CH}_2 \cdot \text{CO}_2\text{Et}) \end{smallmatrix} > \text{CH}$ , b. p. 203—203.5°/16 mm., 215°/28 mm., and 220°/31 mm., is obtained as an oil. If this chloro-pyrimidine is heated with alcoholic ammonia in a sealed tube at 120—130°, the corresponding amino-compound is not produced, but the  $\gamma$ -lactam of 6-amino-2-ethylthiolpyrimidine-5-acetic acid (2-ethylthiol-5:6-*a*-pyrrolidone-pyrimidine) (annexed formula), m. p. 208°, is formed as a red, granular powder, which, on hydrolysis with concentrated hydrochloric acid, is converted into the *hydrochloride* of cytosine-5-acetic acid, which crystallises in minute needles containing  $1H_2O$  and decomposes at 135—140°.

*Cytosine-5-acetic acid*,  $N \begin{smallmatrix} \text{CO} \\ \text{C}(\text{NH}_2) \cdot \text{C}(\text{CH}_2 \cdot \text{CO}_2\text{H}) \end{smallmatrix} \text{NH} \rangle \text{CH}$ , forms colourless crystals, and blackens at  $240-250^\circ$ , but does not melt below  $290^\circ$ ; it is not precipitated by phosphotungstic acid, mercuric chloride, or copper sulphate, but yields an amorphous precipitate with potassium bismuth iodide; the *picrate*, m. p.  $217-218^\circ$ , crystallises in needles.

Thiocarbamide condenses with ethyl formylsuccinate in presence of sodium ethoxide with formation of ethyl 2-thio-6-pyrimidone-5-acetate, together with a small quantity of another crystalline substance, probably 6:6'-*diketo-2:2'-ethylthiol-5:5'-dipyrimidine*,



which decomposes on heating, but has no definite m. p. *Ethyl 2-thio-*

*6-pyrimidone-5-acetate*,  $\text{NH} \begin{smallmatrix} \text{CS} \\ \text{CO} \cdot \text{C}(\text{CH}_2 \cdot \text{CO}_2\text{Et}) \end{smallmatrix} \text{NH} \rangle \text{CH}$ , m. p.  $178-180^\circ$ , and the corresponding *acid*, m. p. about  $260^\circ$  (decomp.), form prismatic crystals.

E. G.

**Pyrimidines. LII. Thiocytosine-5-carboxylic Acid.** TREAT B. JOHNSON and JOSEPH A. AMBLER (*J. Amer. Chem. Soc.*, 1911, 33, 978-985).—It has been shown by Johnson (Abstr., 1910, i, 69) that ethyl  $\alpha$ -cyano- $\beta$ -ethoxyacrylate reacts with ethyl- $\psi$ -thiocarbamide in two ways, yielding a mixture of 5-cyano-2-ethylthiol-6-pyrimidone and ethyl 6-amino-2-ethylthiopyrimidine-5-carboxylate.

A study has now been made of the behaviour of ethyl cyanoethoxyacrylate towards thiocarbamide, and it has been found that condensation takes place with formation of only one compound, namely, ethyl

6-amino-2-thiopyrimidine-5-carboxylate,  $N \begin{smallmatrix} \text{CS} \\ \text{C}(\text{NH}_2) \cdot \text{C}(\text{CO}_2\text{Et}) \end{smallmatrix} \text{NH} \rangle \text{CH}$ ,

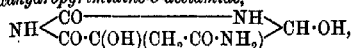
which crystallises in needles and decomposes at  $260-265^\circ$ ; the *hydrochloride* decomposes at  $209-211^\circ$ . On hydrolysing this ester with potassium hydroxide, the corresponding *acid* (2-thiocytosine-5-carboxylic acid) is produced, which forms colourless prisms containing  $1\text{H}_2\text{O}$ , and decomposes at  $253-263^\circ$ . If this acid is boiled for twenty hours with 20% sulphuric acid, it is converted into 2-thio-6-pyrimidone-5-carboxylic

*acid*,  $\text{NH} \begin{smallmatrix} \text{CS} \\ \text{CO} \cdot \text{C}(\text{CO}_2\text{H}) \end{smallmatrix} \text{NH} \rangle \text{CH}$ , m. p.  $246-247^\circ$  (decomp.), which

forms granular crystals. An attempt which was made to desulphurise ethyl 6-amino-2-thiopyrimidine-5-carboxylate by means of chloroacetic acid resulted in the formation of 6-amino-5-carbethoxypyrimidine-2-thioglycollic acid,  $N \begin{smallmatrix} \text{C}(\text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}) \cdot \text{NH} \\ \text{C}(\text{NH}_2) - \text{C}(\text{CO}_2\text{Et}) \end{smallmatrix} \rangle \text{CH}$ , m. p.  $174-177^\circ$  (decomp.), which forms a light brown powder.

When 2:6-dioxypyrimidine-5-acetamide, obtained by heating ethyl 2:6-dioxypyrimidine-5-acetate with ammonia, is treated with bromine in presence of potassium hydroxide, 4:5-dibromo-2:6-dioxyhexahydro-pyrimidine-5-acetamide,  $\text{NH} \begin{smallmatrix} \text{CO} \\ \text{CO} \cdot \text{CBr}(\text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2) \end{smallmatrix} \text{NH} \rangle \text{CHBr}$ , is produced as a light yellow powder; its *picrate* crystallises in yellow needles, and decomposes above  $280^\circ$ . When this compound is warmed

gently with alkali hydroxide, it is transformed into 4:5-dihydroxy-2:6-diketohexahydropyrimidine-5-acetamide,



which forms minute, lemon-yellow prisms, and decomposes at about 270–280°; on reduction with hydriodic acid, it yields 2:6-dioxypyrimidine-5-acetic acid and ammonium iodide. 2:6-Dioxypyrimidine is not reduced at the double bond by hydriodic acid, but can be recovered unchanged after three hours' digestion. E. G.

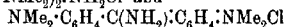
**Hydroxyindazoles.** PAUL FREUNDLER (*Compt. rend.*, 1911, 152, 1256–1259; *Bull. Soc. chim.*, 1911, [iv], 9, 601–605. Compare Abstr., 1903, i, 371; 1904, i, 121, 667, 699; 1906, i, 544).—The position of the chlorine atoms in the 2:5-dichloro-3-hydroxy-2-phenylindazole, previously described (Abstr., 1907, i, 158), has been established by oxidising it with chromic acid, when it yields *benzene-azo-3:5-dichlorobenzoic acid*, red prisms, m. p. 142–143°; sodium hyposulphite converts this into the corresponding diamine. A mixture of phosphorus oxychloride and pentachloride converts the indazole into 2:5:7-trichloro-3-hydroxy-2-phenylindazole,  $\text{C}_{13}\text{H}_7\text{N}_2\text{Cl}_3$ , needles, m. p. 172.5°.

In their general behaviour, hydroxyindazoles resemble phenols, but have feebly basic properties. The foregoing dichloro-compound forms a *potassium salt*, a *methyl ether*, m. p. 144.5°, a *benzoyl derivative*, m. p. 204°, and an *acetyl derivative* occurring in large prisms, m. p. 133°. The *hydrochloride* is hydrolysed by water. Phosphoryl chloride forms a *compound*,  $\text{C}_{13}\text{H}_8\text{ON}_2\text{Cl}_2\text{POCl}_2$ . Sodium hypochlorite in alkaline solution oxidises it to the corresponding azo-acid, but with the formation of an intermediate compound crystallising in green leaflets. W. O. W.

**A Negative Case of Indigotin Condensation.** ELIE E. PISORSCHI (*Bull. Soc. chim.*, 1911, [iv], 9, 548–549).—It was to be expected that 6-nitroveratraldehyde (Pschorr and Sumuleanu, Abstr., 1900, i, 178) would give Baeyer and Drewsen's reaction, condensing with acetone in presence of an alkali to form 5:6:5':6'-tetramethoxyindigotin, but whilst 2-nitroveratraldehyde in this reaction furnishes the corresponding tetramethoxyindigotin, already described by Hayduck (Abstr., 1903, i, 826), the 6-nitroveratraldehyde is recovered unchanged. T. A. H.

**Constitution of Indirubin.** ANDRÉ WAHL and P. BAGARD (*Bull. Soc. chim.*, 1911, [iv], 9, 546–548).—A reply to Maillard (this vol., i, 326). T. A. H.

**Constitution of Auramine.** LEOPOLD SEMPER (*Annalen*, 1911, 381, 234–264).—An attempt is made to decide between the two formulae  $\text{C}(\text{C}_6\text{H}_4\text{NMe}_2)_2\text{NH}_2\text{Cl}$  and



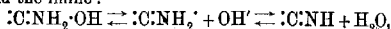
for auramine (compare Graebe, Abstr., 1899, i, 702).

Auramine differs from other dyes with a quinonoid structure in its VOL. C. i.



yellow colour and its general absorption in the blue and violet end of the spectrum, whereas most quinonoid dyes give characteristic absorption bands. A number of acylated auramine bases have been examined, more especially the acetyl derivative, and it is shown that although the bases themselves are pale yellow in colour, they yield deep bluish-violet or bluish-green compounds with acids, metallic haloids, and alkyl haloids. These compounds resemble the quinonoid diphenyl-methane dyes in the following properties: (1) deep colour, (2) selective absorption, (3) instability, and (4) ability to form pale orange-yellow acid salts. The conversion of the bases by acids in either the presence or absence of water into the quinonoid salts is so marked and rapid that they can be used as indicators. These deeply coloured salts derived from acylauramines are so essentially different from the salts of auramine, of methyl- or phenyl-auramine, and of mono-, di- and tri-nitroauramines, that the conclusion is drawn that the latter group of salts cannot have a quinonoid structure, and hence Graebe's imino-structure is accepted.

The gradual change in electrical conductivity observed by Hantzsch and Osswald (Abstr., 1900, i, 256) when an equivalent quantity of alkali is added to a solution of an auramine salt is attributed to the formation of supersaturated solutions and the gradual separation of the excess of solute, and not to the slow conversion of an ammonium base into a carbonium pseudo-base. This conclusion is supported by the fact that the initial conductivity at 25° is greater than at 0°, whereas if the change in conductivity is due to molecular rearrangement, the velocity of the latter should be diminished by fall of temperature, and hence the initial conductivity increased. It is suggested that there is an equilibrium between the imonium base or its ions and the imine:

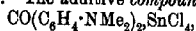


and as the sparingly soluble imine separates, the equilibrium is shifted towards the right. This is supported by the fact that after the crystallisation of the imine is complete, the solution is still yellow, owing to the presence of a small amount of the  $:\text{C}:\text{NH}_2^+$  ion and the colour remains, but can be destroyed by the addition of an appreciable excess of alkali (excess of  $\text{OH}^-$  ions) and restored again by the addition of much water. It is shown that the auramine base is more soluble in dilute sodium chloride solution than in water; when a colourless benzene solution of the imine is shaken with water, the aqueous solution assumes a pale colour, but when sodium chloride solution is used the aqueous layer becomes golden-yellow in colour (compare also Baeyer and Villiger, *Ber.*, 1904, 37, 2852).

Auramine is a strong base, as shown by the fact that it reacts readily with carbon dioxide; the aqueous solution of its carbonate is strongly alkaline, and its trinitro-derivative can form stable salts. This is probably due to the influence of the  $\cdot\text{NMe}_2$ -group on the imino-radicle.

The halochromism of amines (Kauffmann) is more pronounced when the molecule contains a number of unsaturated groups. This can be effected by introduction of olefine linkings, phenyl groups, or auxochromes. The more strongly unsaturated the molecule the deeper is

the colour tone produced by salt formation. The formation of dyes from auramine and Homolka's base by salt formation are examples of halochromism. Further examples are met with in the salts of Michler's ketone, although the salts themselves are too unstable for isolation (compare Staudinger, Abstr., 1909, i, 907; Straus and Bormann, 1910, i, 281). The additive compound,



forms a blood-red precipitate, which turns orange in contact with atmospheric moisture.

A perfectly colourless auramine base, free from carbonate and decomposition products, can be obtained by treating the pure hydrochloride with excess of dilute sodium hydroxide solution and benzene in the cold. The solution is filtered in an atmosphere of hydrogen or nitrogen, and evaporated under reduced pressure, when the base is obtained as a colourless, glistening, crystalline mass. It is not affected by light, and its benzene turns yellow on the addition of a little alcohol. An aqueous-alcoholic solution colours phenolphthalein orange-red. The *perchlorate* forms yellow crystals sparingly soluble in water. Etheral solutions of mercuric chloride or stannic chloride yield yellow precipitates with a benzene solution of the base. The aqueous solution of the hydrochloride does not give an immediate precipitate with silver nitrate, but a precipitate is formed on warming, or on the addition of nitric acid.

Aqueous and alcoholic solutions of auramine salts have a much deeper colour when warm than when cold; magenta and acidified solutions of Michler's ketone behave similarly. An orange-coloured acid hydrochloride has been isolated by the action of excess of hydrogen chloride on the base and drying under reduced pressure. The salt is readily decomposed by the addition of most solvents.

*Acetylauramine*,  $\text{NAc}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ , prepared by the action of acetic anhydride on a benzene solution of the base, crystallises from alcohol in slender, pale yellow needles, m. p.  $221^\circ$ , and turns blue in contact with acids, even with atmospheric carbon dioxide. Its solution in phenol has a moss-green colour, which is removed by the addition of ether.

The quinonoid *hydrochloride*,  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NHAc})\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\cdot\text{Cl}$ , crystallises in glistening, green needles, containing  $1\text{EtOH}$ . Its aqueous solution has a violet-blue colour or in deep layers, a red colour. The salt reacts readily with warm water or acids, yielding Michler's ketone and acetamide, but the primary product in the case of acids is a diacid salt, which has an orange colour and is stable in the presence of excess of acid. With mercuric chloride, acetylauramine yields an additive compound in the form of deep coloured crystals. The *methyl iodide*,  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NMeAc})\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\cdot\text{I}$ , forms a hygroscopic solid, which readily loses methyl iodide; its aqueous and alcoholic solutions have a greenish-blue colour, and its absorption spectrum resembles that of the hydrochloride. With picryl chloride, acetylauramine forms a reddish-violet additive compound, which is readily dissociated. As an indicator, it approaches phenolphthalein, and gives a reaction with a hydron concentration of  $10^{-8}$ . It has the drawback that it is fairly readily decomposed by water or acids, and should, therefore, be added just before the end of the titration.

Benzoylauramine (Finkh and Schwimmer, Abstr., 1895, i, 184) yields a quinonoid chloride,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{NHBz}) \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2 \cdot \text{Cl}$ , in the form of a dark violet, hygroscopic powder.

*Benzenesulphonylauramine*,  $\text{SO}_2\text{Ph} \cdot \text{N} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , crystallises from ethyl acetate in glistening, yellow prisms, m. p.  $183^\circ$ . Its solutions in phenol or glacial acetic acid have a reddish-brown colour, the hydrochloride and oxalate are unstable, and it yields a green compound with stannic chloride.

4-Nitrophenylauramine,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , obtained by heating auramine base with *p*-nitroaniline at  $160^\circ$ , separates from ethyl acetate in dark yellow crystals, m. p.  $226^\circ$ . Its solutions in phenol and glacial acetic acid have a blood-red colour similar to the hydrochloride. 2:4-Dinitrophenylauramine,  $\text{C}_{23}\text{H}_{23}\text{O}_4\text{N}_5$ , obtained by condensing auramine with chloro-2:4-dinitrobenzene in benzene solution, crystallises from amyl alcohol as a brick-red powder. The hydrochloride forms a dark red, hygroscopic mass.

2:4:6-Trinitrophenylauramine,  $\text{C}_{25}\text{H}_{23}\text{O}_6\text{N}_6 \cdot \frac{1}{2}\text{C}_6\text{H}_5$ , forms large, glistening, black prisms, and loses its benzene at  $150^\circ$ . It crystallises from alcohol in glistening, red needles, m. p.  $211^\circ$ , and is only slowly decomposed by acids. The hydrochloride,  $\text{C}_{25}\text{H}_{23}\text{O}_6\text{N}_6\text{Cl}$ , forms glistening, bronzy needles.

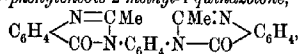
J. J. S.

Quinazolines. XXVII. Synthesis of 3-Aminoaryl-4-quinazolones from Acylantranils and Aromatic Diamines. MARSTON T. BOGERT, ROSS A. GORTNER, and CARL G. AMEND (*J. Amer. Chem. Soc.*, 1911, 33, 949—962).—The work on the synthesis of quinazolines from acylantranils and primary amines (this vol., i, 162, and previous abstracts) has been extended to the aromatic diamines. The condensation in this case is remarkably smooth, and can be best effected by gently fusing a mixture of the reagents. The diamine must possess one primary amino-group, whilst the other may be primary, secondary, or tertiary. The aminoarylquinazolones thus produced, which contain a primary amino-group, are crystalline or pulverulent solids, and when diazotised in the usual way yield diazo- or tetra-azo-compounds, which unite with suitable couplers to form valuable azo-dyes. The following diamines were used: *o*-, *m*-, and *p*-phenylenediamines, 2:4- and 2:5'-tolylenediamines, benzidine, *o*-tolidine, 3-ethoxybenzidine, and di-*o*-anisidine. All these condensed smoothly to form aminoarylquinazolones, except *o*-phenylenediamine. Condensations have also been carried out with di- and poly-amines containing only one primary amino-group. The acylantranils employed were acetylantranil, 5-bromoacetylantranil, 5-nitroacetylantranil, 4- and 5-acetylaminoacetylantranils, benzoylantranil, and *m*- and *p*-nitrobenzoylantranils. The benzoylantranils do not yield aminoarylquinazolones, but diquinazolonyl compounds. In this paper, corrected m. p.'s are recorded in all cases, except where otherwise stated.

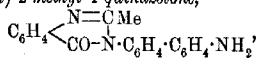
*m*-Nitrobenzoylantranilic acid,  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , m. p.  $233.5^\circ$ , obtained by the action of *m*-nitrobenzoyl chloride on sodium anthranilate, forms colourless prisms. \**p*-Nitrobenzoylantranilic acid, m. p.  $235.5^\circ$ , prepared in a similar manner,

crystallises in nearly colourless needles. *m*-Nitrobenzoylanthranil,  $\text{C}_6\text{H}_4\text{N}(\text{CO})\text{C}_6\text{H}_4\text{NO}_2$ , m. p. 167–168°, forms small, almost colourless needles, and *p*-nitrobenzoylanthranil, m. p. 207°, light yellow needles.

The following compounds were obtained by the condensation of aromatic diamines with acetylanthranil. 3-*m*-Aminophenyl-2-methyl-4-quinazoline,  $\text{C}_6\text{H}_4\text{N}(\text{CO})\text{N}(\text{CMe})\text{C}_6\text{H}_4\text{NH}_2$ , m. p. 210°, from *m*-phenylenediamine. In one experiment, an aqueous solution of *m*-phenylenediamine was treated with acetylanthranil, and the product recrystallised from alcohol. On diluting the mother liquor, another substance, m. p. 158°, separated, which contained 10.22% of nitrogen. 3-*p*-Aminophenyl-2-methyl-4-quinazoline, m. p. 220°, from *p*-phenylenediamine. In one case, this substance was found to be accompanied by a small quantity of 3:3'-phenylenebis-2-methyl-4-quinazoline,



m. p. above 300°. 3-*m*-Aminotolyl-2-methyl-4-quinazoline, m. p. 131.4°, from 2:4-tolylenediamine. Acetylanthranil-*m*-aminotoluidide, m. p. 137–138°, forms stellate groups of colourless needles. 3-*p*-Aminotolyl-2-methyl-4-quinazoline, m. p. 169°, from 2:5-tolylenediamine. 3-(4'-Aminodiphenyl)-2-methyl-4-quinazoline,



m. p. 282–283°, from benzidine. 3-(4'-Aminoditolyl)-2-methyl-4-quinazoline, m. p. 80–81°, from *o*-tolidine. 3-(4'-Aminoethoxydiphenyl)-2-methyl-4-quinazoline,  $\text{C}_6\text{H}_4\text{N}(\text{CO})\text{N}(\text{CMe})\text{C}_6\text{H}_4(\text{OEt})\text{C}_6\text{H}_4\text{NH}_2$

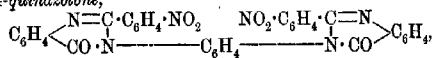
or  $\text{C}_6\text{H}_4\text{N}(\text{CO})\text{N}(\text{CMe})\text{C}_6\text{H}_4\text{C}_6\text{H}_4(\text{OEt})\text{NH}_2$ , m. p. 86–87°, from ethoxybenzidine. 3-(4'-Aminodiansyl)-2-methyl-4-quinazoline, m. p. 72–73°, from *o*-dianisidine.

The following compounds were prepared by condensation with derivatives of acetylanthranil. 6-Bromo-3-*p*-aminodiphenyl-2-methyl-4-quinazoline,  $\text{C}_6\text{H}_4\text{BrN}(\text{CO})\text{N}(\text{CMe})\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{NH}_2$ , m. p. 198–199°, from 5-bromoacetylanthranil and benzidine. 6-Nitro-3-*p*-aminophenyl-2-methyl-4-quinazoline, m. p. 259–260° (decomp.), from 5-nitroacetylanthranil and *p*-phenylenediamine. 6-Acetyl-amino-3-*p*-aminophenyl-2-methyl-4-quinazoline, m. p. 280° (uncorr.), from 3-acetyl-aminoacetylanthranil and *p*-phenylenediamine. 7-Acetyl-amino-3-*m*-aminophenyl-2-methyl-4-quinazoline, m. p. above 310°, from 4-acetyl-aminoacetylanthranil and *m*-phenylenediamine. 7-Acetyl-amino-3-*p*-aminophenyl-2-methyl-4-quinazoline, m. p. above 360°; when this substance is boiled with 20% hydrochloric acid, a purple solution is obtained, which, on treatment with sodium hydroxide, yields 7-amino-3-*p*-aminophenyl-2-methyl-4-quinazoline, m. p. 287°. 7-Acetyl-amino-3-aminotolyl-2-methyl-4-quinazoline, m. p. 290°, from 4-acetyl-aminoacetylanthranil and

2-4-tolylenediamine, yields an *acetyl* derivative, m. p. 268.5°, and when boiled with 10% hydrochloric acid gives 7-amino-3-aminotolyl-2-methyl-4-quinazoline, m. p. 262°. 7-Acetylamino-3-(4'-aminodiphenyl)-

2-methyl-4-quinazoline,  $\text{NHAc} \cdot \text{C}_6\text{H}_4 \begin{smallmatrix} \text{N}=\text{C Me} \\ \text{CO} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \end{smallmatrix}$ , m. p. 296—297°, from 4-acetylaminoacetylanthranil and benzidine; this compound is accompanied by another substance, m. p. 256° (decomp.), which is probably the corresponding diquinazolonyl compound. 7-Acetylamino-3-(4'-aminoditolyl)-2-methyl-4-quinazoline, m. p. 120—125° (decomp.), from 4-acetylaminoacetylanthranil and o-tolidine. 7-Acetylamino-3-(4'-amino-1-ethoxydiphenyl)-2-methyl-4-quinazoline, m. p. about 105—110°, from 4-acetylaminoacetylanthranil and ethoxybenzidine. 7-Acetylamino-3-(4'-aminodiamisyl)-2-methyl-4-quinazoline, m. p. about 144°, from 4-acetylaminoacetylanthranil and di-anisidine, yields a *tetra-acetyl* derivative, m. p. 239°.

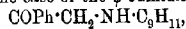
Anschütz, Schmidt, and Greiffenberg (Abstr., 1903, i, 58) have shown that when ammonia is passed into a boiling alcoholic solution of benzoylanthranil, o-benzoylaminobenzamide is produced. It is now found that if benzoylanthranil is boiled with excess of a strong aqueous solution of ammonia, a compound, probably di-o-benzoylaminodibenzamide,  $(\text{NHbz} \cdot \text{C}_6\text{H}_4 \cdot \text{CO})_2\text{NH}$ , m. p. 118°, is formed, which, when boiled with potassium hydroxide solution, is converted into 2-phenyl-4-quinazoline. When benzoylanthranil is heated with *p*-phenetidine, a compound, m. p. 213°, is produced. 3:3'-m-Phenylenebis-2-m-nitrophenyl-4-quinazoline,



m. p. 226°, is obtained by the action of *m*-nitrobenzoylanthranil on *m*-phenylenediamine. The corresponding *p*-nitrophenyl derivative, m. p. 207°, is produced when *p*-nitrobenzoylanthranil is used.

E. G.

**Hydrazones of Phenacylamines.** MAX BUSCH and GEORG HEFELE (*J. pr. Chem.*, 1911, [ii], 83, 425—453).—With the hope of obtaining a direct proof of the stereoisomerism of hydrazones, the evidence for which at present is based chiefly on analogy with the stereoisomerism of the oximes, the authors have prepared hydrazones of amino-ketones of the type  $\text{Ar} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NHR}$ , the *syn*-forms of which, by intramolecular reaction of the hydrazino- and the amino- (or substituted amino-) groups, might be expected to undergo ring closure. Many amino-ketones of the preceding type have been prepared, but only in the case of the  $\psi$ -cumidine derivative,

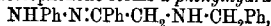


have two forms of the phenylhydrazone been isolated; unfortunately, one form has been obtained in amount so small that the special purpose of the research has not been fulfilled. The phenylhydrazones condense with aldehydes to form tetrahydrotriazines, and are readily oxidised by an excess of the hydrazine or by chromic acid to dihydro-1:2:3-triazoles, which are reduced by sodium and alcohol to tetrahydrotriazoles.

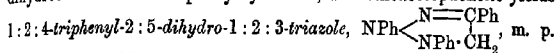
The authors' goal has not been reached by an examination of the semicarbazones and thiosemicarbazones of the preceding amino-ketones; the semicarbazones show a tendency to yield ketotetrahydrotriazines. Only with amino-ketones of the type  $\text{COPh}\cdot\text{CH}_2\cdot\text{NR}_2$  have two forms of the phenylhydrazone been obtained; in these cases, unfortunately, the configurations cannot be determined by the authors' method, because ring closure cannot occur. Phenacylamines,  $\text{COPh}\cdot\text{CH}_2\cdot\text{NHR}$ , are readily obtained by the interaction of  $\omega$ -bromoacetophenone and an amine (2 mols.) in alcoholic solution. The hydrazones are obtained in about 80% yield by adding a small excess of the hydrazine to a suspension of the amino-ketone in cold alcohol containing a little acetic acid and also hydrogen sulphide to prevent the oxidation of the hydrazone to the dihydrotriazole.

The following new compounds have been prepared by the preceding methods.

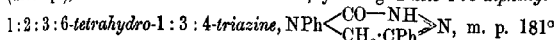
$\omega$ -Benzylaminoacetophenone forms a *phenylhydrazone*,



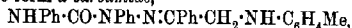
m. p.  $76^\circ$ , an alcoholic solution of which is converted by boiling glacial acetic acid into a *substance*, m. p.  $176^\circ$ , which is probably the dihydrotriazole. With phenylhydrazine,  $\omega$ -anilinoacetophenone yields



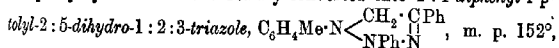
$136.5^\circ$ , whilst with semicarbazide and thiosemicarbazide it yields the *semicarbazone*, m. p.  $171^\circ$  (decomp.), and *thiosemicarbazone*, m. p.  $167^\circ$  (decomp.), respectively; the former forms a *hydrochloride*, m. p.  $230^\circ$  (decomp.), and at  $200^\circ$  loses ammonia, yielding *2-keto-1:5-diphenyl-*



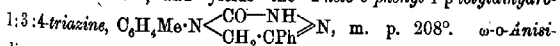
(decomp.).  $\omega$ -*p*-Toluidinoacetophenone forms a *phenylhydrazone*,  $\text{C}_{21}\text{H}_{21}\text{N}_3$ , m. p.  $147^\circ$ , which reacts with phenylcarbimide on the water-bath to form a *carbamide*,



m. p.  $184^\circ$ , and with benzoyl chloride in pyridine, yielding a *benzoyl derivative*,  $\text{NPhBz}\cdot\text{N}:\text{CPh}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ , m. p.  $110^\circ$ . The preceding phenylhydrazone reacts with benzaldehyde at  $120^\circ$  and with salicylaldehyde at  $150^\circ$  to form *substances* (which are probably tetrahydrotriazines), which have various m. p.'s (decomp.) on account of their property of retaining variable quantities of different solvents. The phenylhydrazone is also readily converted into *2:4-diphenyl-1-p-*

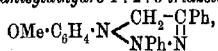


which does not react with phenylcarbimide, aldehydes, nitrous acid, or benzoyl chloride, and is reduced by sodium and alcohol to the *tetrahydrotriazole*,  $\text{C}_{21}\text{H}_{21}\text{N}_3$ , m. p.  $122^\circ$ .  $\omega$ -*p*-Toluidinoacetophenone forms a *semicarbazone*,  $\text{C}_{16}\text{H}_{16}\text{ON}_4$ , m. p.  $182^\circ$  (decomp.), which evolves ammonia at  $205^\circ$ , and yields the *2-keto-5-phenyl-1-p-tolyldihydro-*



*dinoacetophenone*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{COPh}$ , yellow needles, m. p.  $89^\circ$ , forms a *semicarbazone*,  $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_4$ , m. p.  $176^\circ$  (decomp.), and a

phenylhydrazine,  $C_{21}H_{21}ON_3$ , m. p.  $105^\circ$ ; from the latter is obtained the 2:4-diphenyl-1-o-anisylidihydro-1:2:3-triazole,



m. p.  $151.5^\circ$ . The reaction between  $\omega$ -bromoacetophenone and  $p$ -anisidine yields three products:  $\omega$ - $p$ -anisidinoacetophenone, m. p.  $93^\circ$ , yellow leaflets (which differs from all the other phenacylamines by giving a violet coloration with alcoholic ferric chloride), a substance, m. p.  $181^\circ$ , crystallising in orange-yellow plates, and diphenacyl- $p$ -anisidine,  $OMe \cdot C_6H_4 \cdot N(CH_2 \cdot CPh)_2$ , m. p.  $180^\circ$ , yellow needles.  $\omega$ - $p$ -Anisidinoacetophenone forms a semicarbazone, m. p.  $145^\circ$  (decomp.), and an oily phenylhydrazine, from which the corresponding dihydrotriazole,  $C_{21}H_{19}ON_3$ , m. p.  $156^\circ$ , is obtained;  $\omega$ - $p$ -chloroanilinoacetophenone forms a semicarbazone,  $C_{15}H_{17}ON_3Cl$ , m. p.  $167^\circ$  (decomp.), and a phenylhydrazine, m. p.  $147^\circ$ , from which 2:4-diphenyl-1- $p$ -chlorophenyldihydro-1:2:3-triazole,  $C_{20}H_{16}N_3Cl$ , m. p.  $153^\circ$ , is obtained.

$\omega$ - $\psi$ -Cumidinoacetophenone,  $C_6H_2Me_3 \cdot NH \cdot CH_2 \cdot CPh$ , yellow needles, m. p.  $122^\circ$ , forms a semicarbazone, m. p.  $179^\circ$  (decomp.), and a phenylhydrazine, m. p.  $155^\circ$ ; from the mother liquor in the latter preparation a very small amount of a yellow substance, m. p.  $118^\circ$ , is sometimes obtained, which crystallises in rhombohedra, and shows the reactions of a hydrazine. From the phenylhydrazine, m. p.  $155^\circ$ , is obtained 2:4-diphenyl-1- $\psi$ -cumyldihydro-1:2:3-triazole,  $C_{23}H_{23}N_3$ , m. p.  $139^\circ$ .

$\omega$ -Dibenzylaminoacetophenone yields two isomeric phenylhydrazones, which are separated by alcohol; the less soluble form crystallises in colourless leaflets, m. p.  $107^\circ$ , the more soluble in needles, m. p.  $75^\circ$ . The latter change to the former at  $105^\circ$ , or by treating an alcoholic solution of the needles with hydrogen chloride and basifying the resulting hydrochloride, m. p.  $255^\circ$  (decomp.), with ammonia.

$\omega$ -Phenylmethyldiaminoacetophenone forms a phenylhydrazine,  $C_{21}H_{21}N_3$ , m. p.  $98^\circ$ , and a semicarbazone,  $C_{16}H_{18}ON_4$ , m. p.  $202^\circ$  (decomp.).  $\omega$ -Phenylethyldiaminoacetophenone forms, in the absence of air, two isomeric semicarbazones,  $C_{17}H_{20}ON_4$ , one, m. p.  $153^\circ$ , crystallising in leaflets, the other, m. p.  $145^\circ$ , in needles. C. S.

[Preparation of a Carbamide Derivative.] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.P. 231448).—2:2'-Diamino-4:4'-dihydroxy-s-diphenylcarbamide-6:6'-disulphonic acid,



prepared by the action of carbonyl chloride on 2-nitro-4:1-aminophenol-6-sulphonic acid with subsequent reduction is of value in the preparation of azo-dyes. F. M. G. M.

Xanthine Substances from Uric Acid. ERNST EDW. SUNDWIK (Skand. Arch. Physiol., 1911, 25, 256—258. Compare Abstr. 1899, i, 174).—The author finds that calcium urate when heated yields xanthine. A mixture of equal weights of uric acid, calcium formate, and calcium hydroxide is moistened with water until it sets (formation of calcium urate), and the roughly powdered mass is then gradually

heated in a tube in a combustion furnace until evolution of gas begins. The xanthine is precipitated by acidifying the solution of the product, the uric acid removed as acid ammonium urate, and the xanthine finally obtained in the form of its silver nitrate compound.

R. V. S.

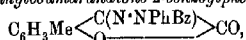
#### Hydroxyazo-compounds and Ketohydrazones. IV—VI.

KARL AUWERS (*Annalen*, 1911, 381, 265—312. Compare Abstr., 1908, i, 477; this vol., i, 168).—The three diketones, 4-methylcoumarandione, thionaphthenquinone, and isatin, yield  $\alpha$ - and  $\beta$ -monophenylhydrazones, and an investigation of these derivatives by the methods already described shows that they possess the hydrazone and not the azo-structure.

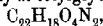
IV. Phenylhydrazone Derivatives of 4-Methylcoumarandione. [With R. APITZ].—The 2-phenylhydrazones of 4-methylcoumarandione

(Fries, Abstr., 1909, i, 175),  $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \diagup \text{C}(\text{N}_2\text{HPh}) \diagdown \\ \text{O} \end{smallmatrix} \text{CO}$ , crystallises

from dilute acetic acid in light yellow needles, m. p.  $148^\circ$ , and dissolves in concentrated sulphuric acid to a brownish-red solution. When left in contact with aqueous-alcoholic sodium hydroxide solution for fifteen to thirty minutes and then acidified, it yields the phenylhydrazone of 4-hydroxy-*m*-tolylglyoxylic acid (Fries and Funck, Abstr., 1909, i, 43), which crystallises from dilute alcohol in greenish-yellow needles, m. p.  $160^\circ$  (decomp.). The same product can be obtained by the action of phenylhydrazine on the ketonic acid, and when heated for five minutes with glacial acetic acid the lactone is re-formed. 4-Methylcoumarandione-2-benzoylphenylhydrazone,



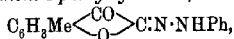
prepared by the action of an aqueous solution of benzoylphenylhydrazine hydrochloride on a methyl-alcoholic solution of the ketone, forms colourless needles, m. p.  $168$ — $169^\circ$ , and yields an orange-yellow solution in concentrated sulphuric acid, and when its solution in ethyl acetate is reduced with zinc dust and glacial acetic acid in the cold, benzanilide is formed, but not aniline. Aqueous alcoholic sodium hydroxide converts the benzoylphenylhydrazone into the benzoyl-phenylhydrazone of 4-hydroxy-*m*-tolylglyoxylic acid,



which forms small, colourless crystals, m. p.  $112^\circ$  (decomp.).

The phenylhydrazone of 4-hydroxy-*m*-tolylglyoxylic acid phenylhydrazone,  $\text{OH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{C}(\text{N}_2\text{HPh}) \cdot \text{CO} \cdot \text{NH} \cdot \text{NHPH}$ , obtained by boiling an alcoholic solution of the 4-methylcoumarandione with an excess of free phenylhydrazine, crystallises in colourless needles, m. p.  $183^\circ$ , and reduces Fehling's solution.

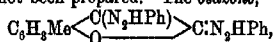
4-Methylcoumarandione-1-phenylhydrazone,



can be prepared by condensing the diketone with benzenediazonium chloride in alkaline or in acetic acid solution, and crystallises from boiling alcohol in golden-yellow plates, m. p.  $224^\circ$ . Its solution in concentrated sulphuric acid has a cherry-red colour. So far acetyl

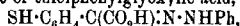


derivatives have not been prepared. The *osazone*,

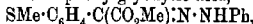


obtained by warming the 1-phenylhydrazone with excess of phenylhydrazine on the water-bath, crystallises from glacial acetic acid in golden-yellow plates, m. p. 223°, and does not reduce Fehling's solution.

V. Phenylhydrazone Derivatives of Thionaphthenquinone. [With KARL MÜLLER.]—Thionaphthenquinone-2-phenylhydrazone (Bezdrík, Friedländer, and Koeniger, Abstr., 1908, i, 201) has m. p. 165–166°, and does not yield an *osazone*. With warm dilute alkalis, it yields the *phenylhydrazone* of thiophenylglyoxylic acid,

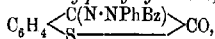


m. p. 80–86°, but this is rapidly transformed into the original phenylhydrazone when warmed with various solvents. The 2-phenylhydrazone of the diketone reacts with methyl iodide and sodium methoxide in the cold, yielding the *dimethyl* derivative of the phenylhydrazone of 2-thiophenylglyoxylic acid,



which crystallises from alcohol in pale yellow, flat needles, m. p. 107–5°. When boiled with sodium hydroxide solution it yields the *monomethyl ether*,  $\text{SMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{N}\cdot\text{NHPh}$ , in the form of sulphur-yellow needles, m. p. 180° (decomp.).

. Thionaphthenquinone-2-benzoylphenylhydrazone,



prepared by condensing the ketone with benzoylphenylhydrazine hydrochloride in hot alcoholic solution, crystallises in brilliant, deep red, flat needles, m. p. 199°. It is readily hydrolysed to the corresponding phenylhydrazone, and when its solution in ethyl acetate is reduced with zinc dust and glacial acetic acid in the cold, no trace of aniline is obtained. Thionaphthenquinone-2-phenylmethylhydrazone,  $\text{C}_{15}\text{H}_{12}\text{ON}_2\text{S}$ , crystallises from alcohol in dark red, glistening needles, m. p. 98–99°. When heated with excess of phenylmethylhydrazine for four hours at 130°, an *isomeride* is obtained, which crystallises in sulphur-yellow prisms, m. p. 122–123°.

Thionaphthenquinone-1-phenylhydrazone,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \text{S} \\ \diagdown \text{S} \diagup \end{array} \text{C:N}\cdot\text{NHPh}$ ,

crystallises in flat, glistening, reddish-brown prisms, has m. p. 194°, and is identical with Friedländer's 1-benzeneazo-2-hydroxythionaphthen (Abstr., 1909, i, 504). It is also formed by condensing phenylhydrazine with the ketodibromide, and with excess of phenylhydrazine at 100° yields the *osazone*,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C}(\text{N}_2\text{HPh}) \\ \text{S} \\ \diagdown \text{S} \diagup \end{array} \text{C:N}_2\text{HPh}$ ,

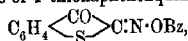
which crystallises from benzene in slender, orange-yellow needles, m. p. 199–200°. The 1-phenylhydrazone reacts with benzoyl chloride in the presence of 2% sodium hydroxide solution, yielding the 1-benzoyl-phenylhydrazone,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \text{S} \\ \diagdown \text{S} \diagup \end{array} \text{C:N}\cdot\text{NPhBz}$ , which exists in two modifications, the one crystallises from glacial acetic acid and a little water in yellow needles or orange-yellow prisms, and has m. p. 156°.

the other crystallises from alcohol in ruby-red rhombs or carmin-red, pointed prisms with a blue shimmer. Both compounds when reduced with zinc dust and glacial acetic acid yield benzanilide, but no trace of aniline.

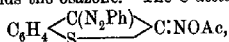
When the 1-phenylhydrazine is methylated by means of methyl sulphate in the presence of sodium hydroxide or of methyl iodide and sodium methoxide, a mixture of *O*- and *N*-methyl derivatives is obtained. *Thionaphthenquinone-1-phenylmethylhydrazone*,  $C_{16}H_{12}ON_2S$ , is sparingly soluble in ether, crystallises from alcohol in long, lustrous, red needles, m. p. 133—134°, and on reduction yields methylaniline. It is also formed when 2-dibromo-3-ketodihydrothionaphthen is condensed with phenylmethylhydrazine. 1-Benzeneazo-2-methoxythionaphthen,  $C_6H_4 \begin{smallmatrix} \text{C(OMe)} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} > \text{C:N:NPh}$ , is readily soluble in ether, and

crystallises in orange-yellow plates, or from glacial acetic acid in carmine-red, pointed needles. Its solutions are mostly golden-yellow coloured, whereas those of the isomeric *N*-methyl derivative have an orange-red colour. When reduced the *O*-ether yields aniline.

The benzoyl derivative of 1-thionaphthenquinoneoxime,



obtained by benzoylating the oxime in the presence of pyridine, crystallises from benzene in glistening, sulphur-yellow prisms, m. p. 170°, and on hydrolysis yields *o*-thiolbenzoic acid. When warmed with phenylhydrazine and glacial acetic acid the benzoyl derivative yields thionaphthenquinone-1-phenylhydrazone. The 2-phenylhydrazone of thionaphthenquinone-1-oxime (D.R.-P. 213458) crystallises from alcohol in glistening, golden-yellow, felted needles, m. p. 172° (not 154°, compare D.R.-P. 213458), and when boiled for five minutes with excess of phenylhydrazine yields the osazone. The *O*-acetate,



crystallises from benzene in compact, golden-yellow prisms, m. p. 156—157°. The corresponding *O*-benzoyl derivative forms golden-yellow, felted needles, m. p. 141—142°.

*Thionaphthenphenylosotriazole*,  $C_6H_4 \begin{smallmatrix} \text{C}_6\text{H}_4 \cdot \text{C:N} \\ \diagup \quad \diagdown \\ \text{S} \quad \text{C:N} \end{smallmatrix} > \text{NPh}$ , obtained by the

action of sodium hydroxide solution on an alcoholic solution of the *O*-acetyl or *O*-benzoyl derivative, forms colourless, glistening needles, m. p. 152°, and is extremely stable.

[With F. ARNDT.]—4-Methylthionaphthenquinone-1-phenylhydrazone,

$C_6H_3Me \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} > \text{C:N}_2\text{HPh}$ , prepared from hydroxy-4-methylthionaphthen (Auwers and Arndt, Abstr., 1909, i, 175) and benzenediazonium chloride in the presence of alkali, crystallises in dark brick-red needles with a strong greenish-yellow shimmer and has m. p. 186.5°.

The benzoyl derivative,  $C_{22}H_{16}O_2N_2S$ , exists in two forms, the one crystallises from alcohol in glistening, orange-yellow needles, m. p. 145°, and the other from benzene and light petroleum in sulphur-yellow prisms, m. p. 157°. By benzoylating in the presence of

pyridine the more readily fusible compound is the chief product. The corresponding 1-oxime,  $C_6H_5Me \begin{smallmatrix} \diagup CO \\ \diagdown S \end{smallmatrix} C:N \cdot OH$ , crystallises in glistening, yellow plates and flat needles, m. p.  $188^\circ$  (decomp., when fairly quickly heated). The dibenzoyl derivative of 4-methyl-2-hydroxy-1-aminothiophen,  $C_6H_5Me \begin{smallmatrix} \diagup O(Bz) \\ \diagdown S \end{smallmatrix} C:NHBz$ , obtained by reducing the oxime and benzoylating the product, crystallises from benzene in colourless plates, m. p.  $233.5^\circ$ .

VI. Isatinphenylhydrazones. — [With A. BOENNECKE.] — Isatin 3-benzoylphenylhydrazone,  $C_6H_4 \begin{smallmatrix} \diagup C(N \cdot NPhBz) \\ \diagdown NH \end{smallmatrix} CO$  or

$$C_6H_4 \begin{smallmatrix} \diagup C(N \cdot NPhBz) \\ \diagdown N \end{smallmatrix} C \cdot OH,$$

obtained by condensing an alkaline solution of isatin with benzoylphenylhydrazine hydrochloride, crystallises from benzene in slender orange-coloured needles, m. p.  $195-196^\circ$ , and with alcoholic sodium hydroxide solution yields the phenylhydrazone and benzoic acid; when reduced with zinc dust and glacial acetic acid, no trace of aniline is obtained.

1-Benzoylisatin-3-phenylhydrazone,  $C_6H_4 \begin{smallmatrix} \diagup C(N_2HPh) \\ \diagdown NBz \end{smallmatrix} CO$ , obtained by benzoylating isatin-3-phenylhydrazone by the Schotten-Baumann method or in the presence of pyridine, crystallises in golden-yellow, felted needles, m. p.  $203^\circ$ , and on reduction with zinc dust and glacial acetic acid yields large quantities of aniline, but no benzanilide. The same benzoyl derivative is formed when *N*-benzoylisatin is condensed with phenylhydrazine.

Isatin- $\beta$ -acetylphenylhydrazone,  $C_{16}H_{13}O_2N_3$ , prepared from isatin and acetylphenylhydrazine, forms small, pale yellow, octahedral crystals, m. p.  $199^\circ$ , and is readily hydrolysed to the 3-phenylhydrazone of isatin (Fischer, Abstr., 1884, 1151). The 1-acetyl-3-phenylhydrazone (Schunck and Marchlewski, Abstr., 1895, i, 288) has m. p.  $132-134^\circ$ , and on reduction yields aniline, but no acetanilide, and is therefore the *N*- and not the *O*-acetyl derivative.

Isatin-2-phenylhydrazone (Heller, Abstr., 1907, i, 442) yields an *N*-benzoyl derivative,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown NBz \end{smallmatrix} C:N_2HPh$ , which crystallises in slender, yellow, felted needles, m. p.  $188-189^\circ$ . It is not hydrolysed by cold alcoholic potassium hydroxide, but when warmed yields the 2-phenylhydrazone, and when reduced yields aniline. J. J. S.

The Diacetyl Reaction for Proteins. ARTHUR HARDEN and DOROTHY NORRIS (*J. Physiol.*, 1911, 42, 332-336). — Acetyl-methyl-carbinol, a product of growth of certain bacteria on sugars, is readily oxidised to diacetyl (dimethyl diketone), which then combines in the presence of alkali with some part of the protein molecule, imparting to the solution a pink colour and green fluorescence. It is now shown that the group in protein on which the reaction depends is  $NH \cdot C(NH_2) \cdot NH \cdot R$ , but the exact significance of *R* has not yet been worked out. Only complex protein substances give any fluorescence,

and this is lost if time is allowed for hydrolysis to occur before the dimethyl diketone is added.

W. D. H.

**Cleavage Products Obtained by the Partial Hydrolysis of Proteins.** EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1911, 72, 1—14).—The fibroin of Canton and Bengal silks was subjected to hydrolysis with 70% sulphuric acid at 25° for four days. It was found that *d*-alanyl-glycine which was obtained in previous experiments on fibroin had been split into its components, but the tripeptide *d*-alanyl-glycyl-*L*-tyrosine, identical with Fischer's synthetic product, was separated out. This is the first instance of a tripeptide actually obtained by protein hydrolysis. From the horny material of the cow's hoof, a polypeptide was similarly obtained, which yielded on further hydrolysis tyrosine, cystine, tryptophan, glutamic acid, and other amino-acids. Another polypeptide, not fully identified, was obtained by the action of trypsin on casein.

W. D. H.

**The Refractive Indices of Solutions of Certain Proteins.** V. GHADIN. T. BRAILSFORD ROBERTSON and J. E. GREAVES (*J. Biol. Chem.*, 1911, 9, 181—184).—The value of  $a$  in the equation  $n - n_1 = ac$ , where  $n$  is the refractive index of the solution of the protein,  $n_1$  that of the solvent, and  $c$  the percentage concentration of the protein, was determined for gliadin in various solvents. In the less highly refractive solvents, the introduction of gliadin increases the refractive index, but in the most highly refractive solvent employed, namely, 75% phenol, the addition of gliadin reduces the refractive index.

W. D. H.

**Hydrolysis of Casein.** THOMAS B. OSBORNE and H. H. GUEST (*J. Biol. Chem.*, 1911, 9, 333—353).—The methods of preparing the casein and estimating its hydrolytic products are given with full details. A table is finally drawn up from the results of the authors and of others of the cleavage products; 36.4% of the nitrogen is still left unaccounted for. The calculations give no evidence that casein differs in constitution to any marked degree from other proteins that do not contain phosphorus.

W. D. H.

**The Composition of Certain Substances Produced by the Action of Pepsin on the Products of the Complete Peptic Hydrolysis of Casein.** T. BRAILSFORD ROBERTSON and H. C. BINDLE (*J. Biol. Chem.*, 1911, 9, 295—302).—The term para-nuclein is adopted for the precipitate obtained when pepsin acts on neutral or faintly acid solutions of caseinates. When this is subjected to partial digestion by weak alkalis, the product obtained is poorer in phosphorus, and is called paranuclein-A. The two contain the same amount of carbon, hydrogen, and nitrogen, and differ from most other proteins by their low content of carbon. The synthetic product obtained at 60—70° by the action of concentrated pepsin on unconcentrated products of complete peptic hydrolysis of casein is identical so far as carbon, hydrogen, and nitrogen are concerned with

para-nuclein. If the products of hydrolysis are concentrated, the synthetic product contains more carbon, but this is attributed to contamination.

W. D. H.

**Substances Accompanying Oxyhæmoglobin in its Crystallisation.** PIERRE THOMAS (*Compt. rend.*, 1911, 152, 1424—1426).—Solvents such as ether, light petroleum, and chloroform extract small quantities of pale coloured substances from crystallised oxyhæmoglobin, but the amount hitherto obtained is insufficient to determine their nature. Light petroleum extracts 0.03—0.04% of a crystalline material, possibly a mixture of cholesterol esters.

W. O. W.

**Reduction of Oxyhæmoglobin.** JULES WOLFF (*Compt. rend.*, 1911, 152, 1332—1334).—Ewald (Abstr., 1907, ii, 184) has stated that the reduction of oxyhæmoglobin by ammonium sulphide is facilitated by the catalase of blood. If this is destroyed, however, by boiling, the liquid still retains the power of accelerating reduction. When the reduced hæmoglobin is shaken with air, re-oxidation occurs, and the process can be repeated a certain number of times until the pigment is destroyed. It has been found, however, that the alternate reduction and oxidation can be repeated indefinitely if, instead of ammonium sulphide, a maceration of Roquefort cheese is used after it has been allowed to grow a bacterial flora by exposure to air. A species of *Coccus* has been isolated from this culture, and found to have a strong reducing action on oxyhæmoglobin.

W. O. W.

**Changes in Physical Condition of Colloids. XI. Imbibition by Gelatin in Acids and Bases.** RICHARD CHIARI (*Biochem. Zeitsch.*, 1911, 33, 167—181).—The experiments were carried out with gelatin, which had been freed from electrolytes by prolonged washing with conductivity water. The plates of gelatin thus treated were exposed to the action of acids and bases, and the amount of water imbibed or lost was determined by weighing the plates. In this way the imbibition grade was determined. If gelatin is purified in the above-mentioned manner, it is extremely sensitive, as regards its imbibition qualities, to acids and bases. A concentration can be determined, in the presence of acids, at which, instead of imbibition, there is a loss of water. The maximum for this loss lies at the isoelectric point of gelatin, at  $2 \cdot 10^{-5}N$ . Acids of different strength, in isohydric concentrations, cause a greater imbibition the smaller their dissociation constant is; thus acetic acid > lactic acid > hydrochloric acid. The deviation of trichloroacetic and sulphuric acids from this rule may be ascribed to the small ionisation of their protein salts, as deduced from viscosity determinations with other proteins. Analogous results were obtained with bases, the weaker bases causing greater imbibition than the stronger bases in isohydroxylic solutions. Amphoteric electrolytes cause smaller imbibition than acids with the same dissociation constants. Theoretical explanations of the results are given, based on Pauli's conception that neutral proteins have a smaller capacity of forming hydrated aggregates than protein salts.

S. B. S.

**Diastases. I. IVAR BANG** (*Biochem. Zeitsch.*, 1911, 32, 417—442).—Ptyalin, after prolonged dialysis, still retains its diastatic power, although very much weakened. This fact can be demonstrated when the reducing sugar is estimated by the author's method. After adsorption by starch, and washing by centrifugalisation the adsorption-product, the ptyalin is still diastatically active. The addition of sodium chloride to the dialysed ptyalin increases its diastatic action. The optimum action of this salt takes place when the quantities added are of about the same order as those found in saliva. The addition of relatively very much larger quantities of sodium chloride does not, however, reduce to any very large extent the diastatic action. Nitrate and sulphate exert a very much less marked action. Disodium hydrogen phosphate also inhibits the action, which can be entirely destroyed if the saliva is dialysed after treatment with the phosphate. The action can, however, be restored again by addition of chloride. This action is explained by assuming that dialysis of saliva does not entirely remove the chloride; if phosphate is added, however, the ptyalin-chloride compound is converted into the corresponding phosphate, and subsequent dialysis then removes all the chloride. Monosodium phosphate in small quantities inhibits only slightly the action of undialysed saliva, but in large quantities it acts strongly; it reactivates dialysed saliva when in small quantities, but to a smaller extent than the chloride; in larger quantities its action again is inhibitory, and this is probably due to the larger hydrogen ion concentration which inhibits ptyalin. This action can be antagonised by addition of the disodium phosphate. Sodium chloride does not act as an activator in presence of lecithin, whereas disodium phosphate does. The monosodium salt acts in the same way as in absence of lecithin. Experiments on the action of saliva under similar conditions to the above (on soluble starch) were carried out on glycogen. In this case the monosodium phosphate was found to exert a strong activating action.

S. B. S.

**Influence of the Viscosity of the Medium on Diastatic Activity.** **PIERRE ACHALME** and **M. BRESSON** (*Compt. rend.*, 1911, 152, 1328—1330).—A close parallelism has been found to exist between the curves showing for aqueous glycerol solutions, (a) variations in the viscosity of the liquid with concentration, and (b) the variations in the rate of hydrolysis of sucrose by invertase at different concentrations of glycerol. The rate of hydrolysis diminishes as the viscosity of the medium increases. Similar results were obtained with emulsin, amylase, trypsin, and organic and inorganic oxydases. That the parallelism is not dependent on the chemical nature of the substance causing viscosity is shown by the fact that mannitol acts in the same way.

W. O. W.

**Role of Viscosity in Variations of the Action of Invertase According to the Concentration of Sucrose.** **PIERRE ACHALME** and **M. BRESSON** (*Compt. rend.*, 1911, 152, 1420—1422. Compare preceding abstract).—A curve showing the variation in viscosity of a sucrose solution with concentration is almost parallel to the curve showing the time necessary for invertase to hydrolyse a definite percentage of the sugar.

W. O. W.

**Viscosity and Diastatic Actions. Hypothesis on the Nature of Diastases.** PIERRE ACHALME (*Compt. rend.*, 1911, 152, 1621—1624. Compare preceding abstracts).—A theoretical paper. The author is led to regard an enzyme in colloidal solution as composed of granules undergoing Brownian movements, and in consequence losing energy as electrons or vibrations in the ether. When the speed of the electrons or the period of the vibrations corresponds with the intramolecular vibration of a substance capable of being acted on by the enzyme, phenomena of resonance occur, bringing about disruption in a similar way to that produced by ultra-violet light. The specific nature of an enzyme depends on accordance of the radiations with the nature of the passive substance. W. O. W.

**Action of Heat on Emulsin.** GABRIEL BERTRAND and ARTHUR COMRON (*Compt. rend.*, 1911, 152, 1518—1521).—Amygdalin was heated for fifteen hours at different temperatures with emulsin. The curve representing the amount of hydrogen cyanide liberated at each temperature is found to be superposable on the curve showing the amount of dextrose, the optimum temperature in each case being about 40°. The curves are no longer superposable, however, if the heating is limited to two hours; the two optimum temperatures under these conditions are 58° and 56° respectively. These observations are held to confirm the view that two distinct diastases are concerned in the hydrolysis of the glucoside, one changing it into a diose and a nitrile, whilst the other effects only fission of the diose. The curves differ from those given by cellulase, and hence this also is a specific enzyme, different from the two foregoing (compare Abstr., 1900, i, 290, 800). W. O. W.

**Is the So-called Peroxydase Actually a Ferment?** HERR and W. D. KOOPER (*Zeitsch. Nahr. Genussm.*, 1911, 21, 385—393).—The results of the authors' experiments lead them to the conclusion that the coloration obtained when milk is treated with Rothenfusser's reagent (guaiacum, *p*-phenylenediamine hydrochloride, and alcohol) is not due to peroxydase, but solely to the presence of alkaline substances in the milk. As soon as the alkaline reaction of these substances is affected by the addition of acids, or mercuric chloride, or by boiling the milk, the latter does not give a coloration with the reagent. When the added acid is neutralised, a coloration is again obtained. The authors have not ascertained definitely whether the alkaline substances consist of calcium-casein compounds or phosphates; probably several substances are present which produce the effect. W. P. S.

**The Inhibitory Action of Inorganic Salts on Catalase.** W. FAVRE (*Biochem. Zeitsch.*, 1911, 33, 32—48).—The influence of the following salts on the action of the catalase of the blood was investigated: sodium chloride and sulphate, potassium chloride and sulphate, magnesium chloride and sulphate, copper chloride and sulphate, ferrous chloride and sulphate, manganese chloride and sulphate; the action of colloidal silver was also investigated. From

the amount of hydrogen peroxide decomposed by the salts, etc., alone and in the presence of catalase, the action of the salts on the catalase itself was determined.

S. B. S.

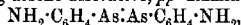
**Derivatives of *p*-Aminophenylarsine Oxide.** ALFRED BERTHEIM (*Ber.*, 1911, 44, 1070—1075. Compare Ehrlich and Berthelm, *Abstr.*, 1910, i, 451).—*p*-Aminophenylarsine dichloride hydrochloride,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsCl}_2\cdot\text{HCl}$ , m. p. 139—140°, is obtained by adding a solution of *p*-aminophenylarsine oxide in cold 2*N*-hydrochloric acid to strongly cooled hydrochloric acid, D 1.19. The corresponding dibromide,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsBr}_2\cdot\text{HBr}$ , m. p. 134°, and diiodide,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsI}_2\cdot\text{HI}$ , are prepared in a similar manner; the latter, a yellow, crystalline powder, forming a colourless solution in water, is also obtained by reducing arsanic acid with hydriodic acid. All three substances volatilise almost without residue, yielding crystalline sublimates (probably compounds of aniline and the arsenic trihalogenide) which are decomposed by water into aniline, arsenious acid, and the halogen acid.

*p*-Acetylaminophenylarsine oxide,  $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}$ , exists in two forms. The one, indistinctly crystalline, anhydrous, and sparingly soluble, is obtained by reducing acetylarsanic acid by hydriodic and sulphurous acids, and has m. p. 288—289° (decomp.). The other, obtained by the action of acetic anhydride on an aqueous suspension of *p*-aminophenylarsine oxide, is crystalline and soluble, contains  $\text{H}_2\text{O}$ , and melts partly at 100° (decomp.), completely at 271°. The anhydrous form is converted into the hydrated form by solution in 2*N*-sodium hydroxide, acidifying with 2*N*-acetic acid, and inoculating the solution with a crystal of the hydrated form. *p*-Acetylaminophenylarsine dichloride hydrochloride,  $2\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{AsCl}_2\cdot\text{HCl}$ , m. p. 137° (decomp.), is obtained by the action of phosphorus trichloride on a suspension of acetylarsanic acid in ethyl acetate; from its solution in sodium hydroxide, acetic acid precipitates the hydrated form, and ammonium chloride the anhydrous form of *p*-acetaminophenylarsine oxide.

C. S.

#### Reduction Products of Arsanic Acid and its Derivatives.

II. *pp'*-Diaminoarsenobenzene. PAUL EHRLICH and ALFRED BERTHEIM [and, in part, E. SCHMITZ] (*Ber.*, 1911, 44, 1260—1269. Compare *Abstr.*, 1910, i, 451).—Arsanic acid can be reduced directly to the corresponding arseno-derivative, *pp'*-diaminoarsenobenzene,



by means of the following reducing agents: (1) Sodium hyposulphite; (2) stannous chloride, alone or in the presence of hydriodic acid as catalyst. An alternative method is to reduce the arsanic acid to *p*-aminophenylarsine oxide (*loc. cit.*), and then to reduce this to the arseno-derivative by means of sodium amalgam, stannous chloride, and hydrochloric acid or sodium hyposulphite. As a rule, the indirect method of reduction yields a purer product. Derivatives of quinquivalent arsenic are more difficult to reduce than those of trivalent arsenic; thus arsenic acids react slowly with a warm solution of sodium hyposulphite or of stannous chloride, whereas the correspond-



ing arsine oxide even in the cold gives an immediate precipitate of the arseno-derivative. This reaction can be made use of for distinguishing between organic arsinic acids and arsine oxides. The arseno-compounds cannot be distilled; many possess colloidal properties. They are extremely reactive, and many undergo rapid oxidation on exposure to the air.

*pp'*-Diaminoarsenobenzene,  $C_{12}H_{12}N_2As_2$ , has m. p.  $260^\circ$ , and is insoluble in most solvents, with the exception of acetic acid and pyridine. It possesses basic properties and yields a hydrochloride,  $C_{12}H_{12}N_2As_2 \cdot 2HCl$ , which decomposes at  $151^\circ$ , and a sparingly soluble sulphate. It reduces ammoniacal solutions of silver nitrate in the cold, and is readily oxidised by alkaline hydrogen peroxide or by an acetic acid suspension of iodine to aminophenylarsinic acid. The arseno-compound can be diazotised, and the resulting diazo-salt, coupled with phenols to azo-dyes. It also yields condensation products with aldehydes and  $\beta$ -naphthaquinonesulphonic acid. When warmed with acids, the arseno-compounds yield strongly coloured products.

The sulphide,  $2C_{12}H_{12}N_2As_2 \cdot H_2SO_3$ , forms a yellow precipitate, very sparingly soluble in the usual solvents.

*p*-Aminophenylarsine oxide and *pp'*-diaminoarsenobenzene have pronounced toxic properties. In the case of rabbits the former is the more active.

J. J. S.

**Preparation of a Nitro-1-aminophenyl-4-arsinic Acid.** FARBWERKE FORM. MEISTER, LUCIUS, and BRÜNING (D. R.-P. 231969).—*Ozanil-4-arsinic acid*,  $CO_2H \cdot CO \cdot NH \cdot C_6H_4 \cdot AsO(OH)_2$ , a crystalline powder, is prepared by heating sodium *p*-aminophenylarsinite (347 parts) with crystalline oxalic acid (378 parts) at  $120$ – $130^\circ$  and subsequently at  $160^\circ$ . When dissolved in concentrated sulphuric acid and treated with nitric acid (D 1.4) in the same solvent (at a temperature not exceeding  $20^\circ$ ), it yields a crystalline paste of *nitro-ozanil-4-arsinic acid*; this is converted by boiling water into *nitro-1-aminophenyl-4-arsinic acid*, yellow needles, which separate as the solution cools.

F. M. G. M.

**Preparation of Soluble Compounds from Hydroxymercuri-carboxylic Acids.** FARBENFABRIKEN FORM. FRIEDR. BAYER & Co. (D.R.P. 229574, 229575, 229781. Compare Abstr., 1910, i, 347, 459).—When sodium diethylbarbiturate is treated with hydroxymercuribenzoic anhydride in aqueous solution and the mixture evaporated, it yields a crystalline neutral compound. The product from hydroxymercuri-*o*-chlorobenzoic anhydride and glutarimide is also crystalline, and the reaction is stated to be applicable to other metals, such as lithium and sodium.

The second and third patents record the preparation of soluble crystalline, double compounds from hydroxymercuri-*m*-hydroxybenzoic anhydride with acetamide, and with alanine; and from hydroxymercuribenzoic anhydride with caffeine, and with asparagine. These products are decomposed by concentrated hydrochloric acid with separation of mercurous chloride.

F. M. G. M.

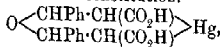
**Complex Mercury Compounds of Cinnamic Acid and its Esters.** WALTHER SCHRAUTH, WALTER SCHÖLLER, and RICHARD STRUENSSEE (*Ber.*, 1911, 44, 1048—1057).—By the use of various alcohols and esters of cinnamic acid, the following complex mercury compounds, and the internal anhydrides obtained therefrom by hydrolysis, have been prepared by the methods already described (*Abstr.*, 1910, i, 347) in order to show that the reaction follows the course previously suggested. *Methyl α-acetoxymercuri-β-ethoxy-β-phenylpropionate*,  $\text{OEt} \cdot \text{CHPh} \cdot \text{CH}(\text{CO}_2\text{Me}) \cdot \text{Hg} \cdot \text{OAc}$ , m. p. 123° (corr.), long needles, forms a *mercurichloride*,  $\text{C}_{12}\text{H}_{15}\text{O}_3\text{HgCl}$ , m. p. 114°, *mercuribromide*, m. p. 85°, and *mercuri-iodide*, m. p. 71°, and yields by hydrolysis the internal anhydride,  $\text{OEt} \cdot \text{CHPh} \cdot \text{CH} \begin{smallmatrix} \diagup \text{CO}_2 \\ \diagdown \text{Hg} \end{smallmatrix}$ , decomp.

191° (corr.). *Methyl α-acetoxymercuri-β-propoxy-β-phenylpropionate*,  $\text{C}_{13}\text{H}_{16}\text{O}_3\text{Hg}$ , m. p. 135·5° (corr.), forms a *mercurichloride*, m. p. 109°, *mercuribromide*, m. p. 84°, *mercuri-iodide*, m. p. 84°, and an internal anhydride, decomp. 188° (corr.). *Methyl α-acetoxymercuri-β-isopropoxy-β-phenylpropionate*, m. p. 150° (corr.), yields the internal anhydride,  $\text{C}_{12}\text{H}_{14}\text{O}_3\text{Hg}$ , decomp. 191° (corr.). *Methyl α-acetoxymercuri-β-isobutoxy-β-phenylpropionate*, m. p. 154° (corr.), yields the internal anhydride,  $\text{C}_{13}\text{H}_{16}\text{O}_3\text{Hg}$ , decomp. 193° (corr.). *Ethyl α-acetoxymercuri-β-methoxy-β-phenylpropionate*, m. p. 107°, and *benzyl α-acetoxymercuri-β-methoxy-β-phenylpropionate*, m. p. 127°, have also been prepared.

A methyl-alcoholic solution of mercuric acetate reacts with allyl cinnamate to form a soluble mercuriacetate, which is precipitated by aqueous sodium chloride as the *dimercurichloride*,

$\text{OMe} \cdot \text{CHPh} \cdot \text{CH}(\text{HgCl}) \cdot \text{CO}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OMe}) \cdot \text{CH}_2 \cdot \text{HgCl}$ , m. p. 169° (decomp.).

The internal anhydride of α-hydroxymercuri-β-methoxy-β-phenylpropionic acid (*loc. cit.*) is moistened with alcohol, suspended in water, and brought into solution by the addition of potassium iodide; by acidifying the solution with *N*-sulphuric acid, a substance,  $\text{C}_{18}\text{H}_{16}\text{O}_3\text{Hg}$ , m. p. 200° decomp., is obtained, which acts as a dibasic acid and does not yield mercuric sulphide by treatment with ammonium sulphide. Probably it has the constitution.



C. S.

**Stannous Alkyl Derivatives. I.** PAUL PFEIFFER (*Ber.*, 1911, 44, 1269—1274. Compare Löwig, *Annalen*, 1852, 84, 320; Frankland, *ibid.*, 1853, 85, 329).—[With R. PRADÉ].—Pure tin diethyl is most readily prepared by reducing tin diethyl chloride with 4% sodium amalgam and ether, and filtering rapidly, all the work being carried on in an atmosphere of hydrogen. It forms a pale yellow, odourless oil, and decomposes when distilled under reduced pressure. It combines readily with oxygen, yielding a white, amorphous precipitate of the oxide,  $\text{SnEt}_2\text{O}$ . It also combines readily with chlorine, bromine, or iodine, and with ethyl iodide at 140° yields tin triethyl iodide.

[With H. REKATE].—Nearly pure tin diethyl can be obtained by

the action of a large excess of magnesium ethyl bromide on stannous chloride, provided the Grignard reagent is free from alkyl iodide.

J. J. S.

**Hexaphenylsilicoethane and Some Biphenyl-substitution Products of Ordinary Ethane and Ethylene.** WILHELM SCHLENK, JULIUS RENNING, and GEORGE RACKY (*Ber.*, 1911, 44, 1178—1182).—The action of metals on triphenylsilyl chloride has been investigated, in the hope of obtaining the silicon analogue of triphenylmethyl.

The metals usually employed for the removal of halogen in the preparation of triphenylmethyl are without action on triphenylsilyl chloride. The removal of chlorine from the latter compound may, however, be effected by heating it with sodium in xylene solution. The *hexaphenylsilicoethane*,  $\text{SiPh}_6\cdot\text{SiPh}_6$ , thus obtained, crystallises in slender prisms, m. p. about  $354^\circ$ . It shows no tendency to dissociate, and remains unchanged when subjected to the action of oxygen in hot xylene solution. From its stability the conclusion is drawn that the total valency of the silicon atom is greater than that of the carbon atom.

Triphenylsilyl chloride does not form coloured additive products, and remains colourless in contact with phenol. The *sodium* derivative of triphenylsilyl is obtained in a crystalline condition by heating the silyl with sodium in toluene solution.

It has previously been shown that the introduction of phenyl groups into hexaphenylethane greatly increases the tendency to dissociation. In order to ascertain if a similar influence is to be observed in the case of tetraphenylethane and tetraphenylethylene, the authors have prepared and examined the behaviour of some tetraphenyl derivatives of these hydrocarbons; no evidence of dissociation was obtained.

*ω*-Bromo-di-4-diphenylmethane,  $\text{CHBr}(\text{C}_6\text{H}_4\text{Ph})_2$ , prepared by brominating di-4-diphenylmethane (Weiler, this Journ., 1875, 151) at  $185^\circ$ , crystallises in colourless leaflets, m. p.  $143^\circ$ ; it gives a red (in thin layers, blue) coloration with strong sulphuric acid, and is converted by aqueous potassium hydroxide into *di-p-phenylbenzhydrol*,  $\text{CH}(\text{C}_6\text{H}_4\text{Ph})_2\cdot\text{OH}$ , leaflets or needles, m. p.  $150^\circ$ . When heated with copper-bronze in xylene solution, it yields *s-tetra-4-diphenylethane*,  $\text{CH}(\text{C}_6\text{H}_4\text{Ph})_2\cdot\text{CH}(\text{C}_6\text{H}_4\text{Ph})_2$ . This forms short prisms, m. p.  $276\text{--}279^\circ$ , and crystallises from benzene and xylene with one molecule of the solvent. Its solutions in solvents of high boiling point are colourless, do not decolorise iodine, and are unattacked by oxygen, so that no dissociation takes place. *Tetra-4-diphenylethylene*,  $\text{C}(\text{C}_6\text{H}_4\text{Ph})_2\cdot\text{C}(\text{C}_6\text{H}_4\text{Ph})_2$ , prepared by heating *ω*-bromodi-4-diphenylmethane above its melting point, crystallises in pale yellow needles, m. p.  $330^\circ$ . F. B.

## Organic Chemistry.

$\Delta^{\alpha\alpha}$ -Undecadiene and  $\Delta^{\alpha\alpha}$ -Hexadecadiene. J. N. REFORMATSKY, E. (FRISCHKEWITSCH-FROCHIMOWSKY, and A. SEMENZOFF (*Ber.*, 1911, 44, 1885—1886).—A mixture of undecadiene and hexadecadiene is obtained on adding magnesium ribbon to  $\alpha\alpha$ -dibromopentane in ethereal solution, and subsequently boiling with allyl bromide. The hydrocarbons were fractionally distilled under reduced pressure over metallic sodium.

$\Delta^{\alpha\alpha}$ -Undecadiene,  $C_{11}H_{20}$ , is a colourless, mobile liquid, b. p.  $187^{\circ}/755$  mm. (corr.),  $D_4^{20}$  0.7671,  $n_D^{20}$  1.43497. It decolorises 4 atoms of bromine in ethereal solution, forming a viscid, colourless tetrabromide.

$\Delta^{\alpha\alpha}$ -Hexadecadiene,  $C_{16}H_{30}$ , is a colourless, mobile liquid, solidifying to a mass of crystalline leaflets, m. p.  $-14^{\circ}$  to  $-12^{\circ}$ , b. p.  $142-147^{\circ}/6$  mm.,  $D_4^{20}$  0.8149,  $n_D^{18}$  1.45612. It forms a viscid, faintly red-coloured tetrabromide.

Both hydrocarbons form bright green additive products with liquid nitrogen trioxide.  $\Delta^{\alpha\beta}$ -Dodecadiene and dimethyldodecadiene have been prepared in a similar manner. E. F. A.

Preparation of Chloro- and Bromo-compounds from Organic Bases. JULIUS VON BRAUN and W. SOBECKI (*Ber.*, 1911, 44, 1464—1475. Compare Abstr., 1904, i, 731, 841; 1905, i, 206, 341, 596, 634; 1907, i, 79; 1910, i, 25, 119).—A simple method for the preparation of an alkyl chloride,  $RCl$ , from an amine,  $R\cdot NH_2$ , is to benzoylate the amine and to decompose this according to the equation:  $R\cdot NH\cdot C(=O)Ph + PCl_5 = POCl_3 + PhCN + RCl$ . This reaction does not proceed quantitatively, and only 60—75% of benzonitrile is formed as a rule. After removing the phosphoryl chloride by means of water, the benzonitrile and alkyl chloride can be separated in certain cases by fractional distillation. If, however, the boiling points are too close for such a separation, the mixture is treated with a slight excess of ethyl alcohol and one equivalent of hydrogen chloride, and on the addition of ether the crystalline benzimino-ethyl ether hydrochloride is completely precipitated at the end of four days.

The following compounds have been prepared by this method:  $\alpha$ -Phenylamyl chloride, 73% (Abstr., 1910, i, 844);  $\alpha\gamma$ -dibromoheptane, 65% (Abstr., 1906, i, 577), and  $\alpha\alpha$ -dichloropentane. The method is much more convenient than the old one of removing the benzonitrile by hydrolysis to benzoic acid. Nonyl bromide is readily obtained from octyl iodide, by converting the latter into the cyanide, reducing with sodium and alcohol to nonylamine, and then treating according to the general method. Nonylamine has b. p.  $201^{\circ}$ , and rapidly absorbs moisture and carbon dioxide (compare Hofmann, Abstr., 1882, 1054). It is not identical with the nonylamine prepared from petroleum by Pelouze and Cahours (*Jahres.*, 1863, 529). The hydrochloride crystallises well and is not hygroscopic; the *platinichloride*,  $C_{15}H_{33}N_2Cl_6Pt$ , forms a pale yellow precipitate, and decomposes at  $205-207^{\circ}$ ; the

*picrate*,  $C_{15}H_{24}O_6N_4$ , crystallises from alcohol in brilliant needles, m. p.  $111^\circ$ , and the *benzoyl* derivative,  $C_{18}H_{30}ON$ , is readily soluble in alcohol and has m. p.  $49^\circ$ . *Nonyl bromide*,  $C_9H_{19}Br$ , is a colourless liquid, b. p.  $91^\circ/9$  mm. With magnesium and carbon dioxide in the presence of dry ether, it yields decolic acid together with octadecane.

Pentadecyl chloride can be obtained from palmitic acid by transforming the latter into its amide, and conversion of this into pentadecylamine, the *benzoyl* derivative of which has m. p.  $78^\circ$ . *Pentadecyl chloride*,  $C_{15}H_{31}Cl$ , is an oil with b. p.  $168-171^\circ/10$  mm., and on treatment with aniline yields pentadecylaniline (Lé Sueur, *Trans.*, 1910, 97, 2433).

Heptadecyl chloride can also be obtained from cetyl iodide by conversion into the nitrile, reduction of this with sodium and alcohol, and treatment of the benzoyl derivative of the resulting amine with phosphorus pentachloride. *Cetyl cyanide* [*heptadecanitrile*],  $C_{16}H_{33}CN$ , has b. p.  $208^\circ/10$  mm., and m. p.  $29^\circ$ . Heptadecylamine has b. p.  $322-324^\circ$  and m. p.  $48^\circ$ , and *heptadecyl chloride*,  $C_{17}H_{35}Cl$ , b. p.  $192-195^\circ/10$  mm. and m. p.  $24^\circ$ .

$\alpha\mu$ -Dichlorododecane can be obtained from  $\alpha\kappa$ -diiodododecane (*Abstr.*, 1910, i, 26) by a similar method. When the dibenzoyl derivative of  $\alpha\mu$ -diaminododecamethane (*loc. cit.*) is distilled with phosphorus pentachloride under reduced pressure, and the products decomposed with water,  $\alpha\mu$ -dichlorododecane,  $C_{12}H_{24}Cl_2$ , is obtained as an oil, b. p.  $170-172^\circ/10$  mm., which solidifies and then has m. p.  $29^\circ$ . With sodium phenoxide and alcohol it yields  $\alpha\mu$ -diphenoxydodecane, m. p.  $86^\circ$ . A by-product obtained during the distillation of the dichloro derivative is  $\mu$ -chlorododecylbenzamide,  $CH_2Cl(CH_2)_{11}\cdot NH\cdot COPh$ , which crystallises from a mixture of ether and light petroleum in brilliant plates, m. p.  $66^\circ$ .

J. J. S.

**Preparation of Olefine Alcohols of the General Formula  $OH\cdot CHMe\cdot CR\cdot CH_2$ .** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 233519).—It is found that unsaturated  $\alpha\beta$ -ketones can be readily converted into the therapeutically valuable olefine alcohols of the general formula  $OH\cdot CHMe\cdot CR\cdot CH_2$  (where R is hydrogen or an alkyl group) by a series of operations represented by the following equations:



(2)  $\text{COMe}\cdot\text{CHR}\cdot\text{CH}_2\cdot\text{NMe}_2 + \text{H}_2 = \text{OH}\cdot\text{CHMe}\cdot\text{CHR}\cdot\text{CH}_2\cdot\text{NMe}_2$ , this on methylation and subsequent treatment with silver hydroxide yields  $\text{OH}\cdot\text{CHMe}\cdot\text{CHR}\cdot\text{CH}_2\cdot\text{NMe}_2\cdot\text{OH}$ , which is readily decomposed by heat into water, trimethylamine, and the required alcohol.

$\beta$ -Methyl- $\Delta^2$  buten- $\gamma$ -ol,  $\text{OH}\cdot\text{CHMe}\cdot\text{CMe}\cdot\text{CH}_2$ , a colourless oil, b. p.  $113-115^\circ$ , sparingly soluble in water, which on oxidation with chromic acid yields the characteristic odour of ethyl vinyl ketone, was obtained by means of the following intermediate compounds:  $\beta$ -Methyl- $\Delta^2$ -buten- $\gamma$ -one,  $\text{COMe}\cdot\text{CMe}\cdot\text{CH}_2$ , was converted by dimethylamine into dimethyl- $\beta$ -acetylpropylamine,  $\text{CHMeAc}\cdot\text{CH}_2\cdot\text{NMe}_2$ , b. p.  $51-51.5^\circ/13$  mm., a colourless oil readily soluble in water; this on reduction with sodium amalgam or electrolysis yielded  $\delta$ -dimethylamino- $\gamma$ -methylbutan- $\beta$ -ol,  $\text{OH}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{NMe}_2$ , a colourless, soluble

oil, b. p. 64–66°/16 mm., or 166–167° under atmospheric pressure; the *methiodide*, m. p. 154°, furnished, on treatment with silver hydroxide, a syrupy *base*, which decomposed at 140–160° into the required  $\beta$ -methyl- $\Delta^2$ -buten- $\gamma$ -ol. Methyl vinyl ketone,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}:\text{CH}_2$ , on treatment with dimethylamine yielded  $\delta$ -dimethylamino- $\beta$ -butanone,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_2$ , b. p. 39–45°/14 mm., a colourless oil readily soluble in water, which on reduction furnished  $\delta$ -dimethylamino- $\beta$ -butanol,  $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_2$ , b. p. 150–155°, a soluble oil with an odour of piperidine, and was subsequently converted into methylvinylcarbinol,  $\text{OH}\cdot\text{CHMe}\cdot\text{CH}:\text{CH}_2$ , b. p. 98–100°, a colourless oil sparingly soluble in water.

F. M. G. M.

**Beeswax. III. Are the Alcohols from Psyllawax and Beeswax Identical?** ERNST EDW. SUNDWIK (*Zeitsch. physiol. Chem.*, 1911, 72, 455–458. Compare Abstr., 1899, i, 112; 1907, i, 887).—It is shown that the alcohol from beeswax is not identical with psylla alcohol. When the latter is heated with soda-lime at 360–370°, psyllic acid is formed, whereas the same acid cannot be obtained from the alcohol of beeswax.

Beeswax alcohol and soda lime at 320° yield a compound containing C = 84.05 and H = 14.60%;  $(\text{C}_{38}\text{H}_{67})_2\text{O}$  or  $(\text{C}_{38}\text{H}_{66})_2\text{CO}$ ? It crystallises from acetone, has m. p. 56–56.5°, and b. p. 310–314°. The alcohol and soda lime at 220–260° yield a small amount of an acid with m. p. 78°. The *silver* salt gave Ag = 17.53%.

J. J. S.

**Acid Sodium Acetates.** RYUJI ABE (*Mem. Coll. Sci. Eng. Kyōto*, 1911, 3, 13–17. Compare Vaselieff, Abstr., 1909, i, 756).—The solubility of sodium acetate in acetic acid solutions at 20° has been determined, also the composition of the residues, and the conditions under which the hydrated salt as well as the acid salts come into existence found to be as follows:

Molecular percentage in solution.		Residue.
$\text{NaC}_2\text{H}_3\text{O}_2$	$\text{C}_2\text{H}_4\text{O}_2$	
9.5	0	} $\text{NaC}_2\text{H}_3\text{O}_2, 8\text{H}_2\text{O}$ .
10.82	8.28	
10.84	32.90	} $\text{NaC}_2\text{H}_3\text{O}_2, \text{C}_2\text{H}_4\text{O}_2$ .
—	—	
		} $\text{NaC}_2\text{H}_3\text{O}_2, 2\text{C}_2\text{H}_4\text{O}_2$ .

J. D. K.

**Solubility of Strontium Acetate and the Transition Point of its Hydrates.** YUKICHI OSAKA and RYUJI ABE (*Mem. Coll. Sci. Eng. Kyōto*, 1911, 3, 51–54).—Strontium acetate is well known to crystallise with  $\frac{1}{2}\text{H}_2\text{O}$  at 15°, but with  $4\text{H}_2\text{O}$  at lower temperatures. The solubility has been determined between 0° and 97°, and the transition point found to be 9.4°. Above this temperature the solubility decreases, and seems to reach a minimum at about 83°. The crystals, stable at lower temperatures, were difficult to free completely from the mother liquor on account of their instability at the ordinary temperature. A small quantity of strontium chloride was therefore

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added to the solution, and the amount of mother-liquor adhering to the crystals taken for analysis was estimated from their chloride content.

J. D. K.

**Catalytic Preparation in the Wet Way of Esters of Saturated Aliphatic Acids.** JEAN B. SENDERENS and J. ABOULENE (Compt. rend., 1911, 152, 1671—1673. Compare Abstr., 1910, i, 649, 651).—Two hundred c.c. of a mixture of acetic acid and alcohol in equimolecular proportions give on distillation a liquid containing 17.8% of the theoretical amount of ethyl acetate, whereas under the same conditions, but in presence of 10 grams of anhydrous aluminium sulphate or potassium hydrogen sulphate, the yield of ester is 82%. With 1% of sulphuric acid by volume, the yield is 86.5%. The catalytic effect of the latter is attributed to the formation of ethyl hydrogen sulphate; this becomes converted into the relatively unstable ethyl sulphate, which reacts with acetic acid to form the ester and ethyl hydrogen sulphate. The latter is the actual catalyst and not the sulphuric acid. Anhydrous sodium sulphate is without catalytic effect on esterification, and hence the reaction is not entirely dependent on the efficiency of the catalyst as a dehydrating agent.

W. O. W.

**Ethyl Acetate.** A. KURTENACKER and H. HABERMANN (*J. pr. Chem.*, 1911, [ii], 83, 541—552).—Continuing the experiments of Habermann and Brezina (Abstr., 1909, i, 873), the authors have investigated the formation of ethyl acetate from 96 volume % alcohol and glacial acetic acid in the presence of sodium metaphosphate, or the ignited sulphate of copper, magnesium, nickel, zinc or sodium as the dehydrating agent. A mixture of the alcohol and the acid in approximately molecular proportions is kept for some hours with a quantity of the dehydrating agent in excess of that required to combine with the water produced in the reaction; the whole is then heated for many hours under a reflux condenser, the course of the reaction being followed by siphoning off samples at intervals, cooling, filtering, and titrating the residual acetic acid with  $N/2$ -sodium hydroxide. Sodium metaphosphate or sodium sulphate has no influence whatever on the yield of ethyl acetate; copper sulphate, zinc sulphate, and magnesium sulphate produce approximately the same effect; nickel sulphate is by far the best dehydrating agent. Having shown that an excess of alcohol or the prolonged heating of the mixture does not improve the yield of purified ethyl acetate, the authors state the following as the best conditions for the preparation of the ester.

A mixture of 200 grams of alcohol, 250 grams of acetic acid, and about 160 grams of anhydrous nickel sulphate is distilled until the temperature begins to exceed  $73^{\circ}$ . The condenser is then arranged vertically, and the mixture is heated under reflux, until the b. p. has fallen below  $73^{\circ}$ . The condenser is then reverted, and the mixture again distilled until the temperature begins to exceed  $73^{\circ}$ . These operations are repeated as long as any liquid distils over below  $73^{\circ}$ . The distillate containing a molecular compound of ethyl alcohol and ethyl acetate, b. p. about  $72^{\circ}$  (*loc. cit.*), is purified in the usual way.

C. S.

**Preparation of Esters of Organic Acids with the Exception of those of Formic Acid.** ADMINISTRATION DER MINEN VON BUCHSWEILER AKT.-GES. (D.R.-P. 232818).—It is found that esters can be prepared in quantitative yield by boiling the components together in the presence of anhydrous calcium chloride and a mineral acid; the ester rises to the surface of the liquid, and is thus readily separated from the hydrated calcium chloride. Details for the preparation of ethyl and amyl acetates, methyl butyrate, ethyl benzoate, and ethyl phthalate are given in the patent. F. M. G. M.

**Preparation of Tri-iodo-derivatives of Stearic Acid.** ERNST ERDMANN (D.R.-P. 233893).—Tri-iodostearic acid derivatives may be obtained by the action of three molecules of iodine monobromide or monochloride or hydrogen iodide in acetic acid on a cooled solution of linoleic acid in the same solvent; excess of halogen is removed with sulphurous acid, the product separated by stirring in petroleum, and then crystallised from acetic acid.

*Tribromotri-iodostearic acid* has m. p. 122–124°, and by shaking with calcium hydroxide is converted into its calcium salt.

*Trichlorotri-iodostearic acid* is a colourless, crystalline powder, m. p. 144°.

*Tri-iodostearic acid* is obtained when hydrogen iodide is employed, and forms a calcium salt. F. M. G. M.

**Preparation of Unsaturated Dihalogenated Aliphatic Acid Chlorides.** F. HOFFMANN-LA ROCHE & Co. (D.R.-P. 232459).—It is found that the hitherto unknown unsaturated dihalogenated aliphatic acid chlorides of the general formula  $C_nH_{2n-4}X_2O_2$  ( $X = \text{halogen}$ ) can be prepared in quantitative yield by the action of thionyl chloride on the corresponding dihalogenated acid.

*Di-iodostearoyl chloride* is thus obtained from di-iodostearolic acid (Liebermann and Sachse, Abstr., 1892, i, 470); it forms a yellow oil, which can be distilled under 0.3 mm. pressure without decomposition; the corresponding *dibromostearoyl chloride* is a pale brown, oily fluid, which solidifies at the temperature produced by a mixture of solid carbon dioxide and ether.

*Di-iodotaririoyl chloride* forms brownish-yellow, spear-shaped crystals, m. p. 28°.

*Di-iodobhenoyl chloride* has m. p. 19°.

F. M. G. M.

**Preparation of Stable Bromo- and Iodo-derivatives of Fats Free from Sulphur.** ARNOLD VOSWINKEL (D.R.-P. 233857).—Animal and vegetable oils can be conveniently halogenated in alcoholic solution by means of the reaction occurring between chloral hydrosulphide and bromine (or iodine) according to the equation  $(C_2H_5O)_2H_2S + 2I = 2HI + S + 2C_2H_5O$ , when the halogen acid formed at once attacks the oil.

Sesame oil under these conditions yielded a yellow, oily product containing 4–5% iodine.



*Butylchloral hydrosulphide*, obtained by passing hydrogen sulphide into a solution of butylchloral in chloroform, forms leaflets, m. p. 85°.

These oils containing bromine and iodine are therapeutically active.

F. M. G. M.

"Alcoholysis" of Japan Wax. EUGÈNE TASSILLY (*Bull. Soc. chim.*, 1911, [iv], 9, 608—615. Compare Geitel and van der Want, *Abstr.*, 1900, i, 271, Schaal, *Abstr.*, 1908, i, 3, and Matthes and Heintz, *Abstr.*, 1910, i, 149).—The author has examined the acids furnished by Japan wax when "alcoholysed" by Haller's process (*Abstr.*, 1907, i, 9). It was found necessary to add sufficient ether to keep the material in solution, and under these conditions the process had to be continued thirteen hours to effect complete hydrolysis.

The wax consists principally of palmitin, and by Haller's method a yield of 55% of pure methyl palmitate is readily obtained from it. Other acid constituents detected in the course of the present investigation were pelargonic, stearic, oleic, and japaic acids, and an acid,  $C_{12}H_{20}O_2$  (or  $C_{30}H_{58}O_4$ ), m. p. 87°, with acids soluble in water and possibly including some isobutyric acid. No arachidic acid was found. The unsaponifiable matter amounted to 0.54%.

T. A. II.

Keto-enolic Equilibrium of Ethyl Acetoacetate. ARTHUR HANTZSCH (*Ber.*, 1911, 44, 1771—1776).—Correction of mistakes in, and a more extended discussion of, work already recorded (*Abstr.*, 1910, i, 811; compare also Meyer, this vol., i, 351; Knorr, *ibid.*, i, 516).

C. S.

Neutralisation Curve of Oxalic Acid. J. E. ENKLAAR (*Chem. Weekblad*, 1911, 8, 487—492).—A table is given containing the results of measurements with the gas electrode, obtained in the step-by-step neutralisation of solutions of oxalic acid with sodium hydroxide. A curve is appended showing the relation of the concentration of the hydrogen ions to the quantity of added alkali.

A. J. W.

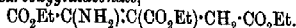
Improved Method of Preparation of Mono-substituted Malonic and Acetoacetic Esters. HERMANN LEUCHS (*Ber.*, 1911, 44, 1507—1511).—The formation of the disubstituted ethyl malonate, which is usually obtained as a by-product in the preparation of the mono-substituted ester, can be prevented to a great extent by employing a large excess, usually 1 mol., of ethyl malonate. Thus the following substances have been prepared, the figures in the brackets denoting the yield by the ordinary method: ethyl benzylmalonate, 85% (50—55%); ethyl  $\gamma$ -phenoxyethylmalonate, 89% (55%: Fischer and Blumenthal, *Abstr.*, 1907, i, 191); ethyl  $\delta$ -chloro- $\gamma$ -valerolactone- $\alpha$ -carboxylate, 78% (50%: Traube and Lehmann, *Abstr.*, 1901, i, 501); ethyl  $\gamma$ -bromopropylmalonate, 35—38% (25%: Willstätter and Ettlinger, *Abstr.*, 1903, i, 362).

Similarly, by using an excess of ethyl acetoacetate, ethyl benzylacetoacetate has been obtained in 89% yield (55%), and acetyl- $\delta$ -chlorovalerolactone in 74% yield (50%: Traube, *loc. cit.*).

C. S.

**Ethyl Oxalysuccinate.** WILHELM WISLICENUS and MARTIN WALDMÜLLER (*Ber.*, 1911, 44, 1564—1573).—An ether-alcohol solution of potassium ethoxide reacts with ethyl oxalate to form insoluble ethyl potassio-oxalysuccinate; this crystallises in very slender, matted needles. On acidifying, the ester is obtained as a colourless oil; it exists in two forms in equilibrium, the enolic, giving a deep red and the ketonic, showing no coloration with ferric chloride. Of the solvents methyl and ethyl alcohols, ether and benzene, the first named contains least, and the last most, of the enolic modification.

With ammonia, ethyl oxalysuccinate forms a neutral crystalline salt-like additive product, which sinters at 82°, m. p. 88—89°. This substance changes spontaneously, or more quickly on warming, to ethyl  $\alpha$ -amino- $\beta$ -carboxyglutamate,



This crystallises in colourless, lustrous plates, m. p. 68—69°, b. p. 255—260°/112 mm. or 211—214°/27 mm.

The ammonia compound interacts with copper acetate, forming ethyl cupro-oxalysuccinate, crystallising in slender, green needles, m. p. 64—69°. The corresponding nickel compound forms greenish-white needles, m. p. 114—119°; the zinc compound separates in colourless needles.

Ethyl oxalysuccinate phenylhydrazine separates in small, pale yellow crystals, m. p. 85°. At 150°, or on treatment with hydrogen chloride in ethereal solution, ethyl 3-carboxy-1-phenyl-5-pyrazolone-4-acetate is obtained. This forms an acetyl derivative crystallising in colourless needles, m. p. 89—90°. The corresponding acid phenylpyrazolone, obtained by hydrolysis of the ester, is converted by acetyl chloride into the anhydride of 3-carboxy-1-phenyl-5-acetoxypyrazole-4-acetic acid,  $\text{C}(\text{O}\cdot\text{COMe})\cdot\text{C}\cdot\text{CH}_2\cdot\text{CO}$   
 $\text{NPh}\text{---}\text{N}\cdot\text{C}\cdot\text{CO}\cdot\text{O}$ , which crystallises in lustrous, colourless needles, m. p. 150—151°.

On boiling with alkali and acidifying, 3-carboxy-1-phenylpyrazolone-4-acetic acid, m. p. 232°, is obtained. On boiling with alcohol and precipitating with water, the mono-ethyl ester of the acetylated acid is obtained in colourless, lustrous needles, m. p. 178—182°.

Ethyl oxalysuccinate forms a crystalline additive product with diphenylhydrazine, m. p. 78—79°; on keeping, this changes into the diphenylhydrazine, which is an oil.

With hydroxylamine an additive product consisting of 2 mols. of ester and 1 mol. of hydroxylamine is obtained; it crystallises in slender, colourless needles, which soften at 55°, m. p. 61—62°.

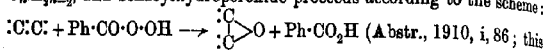
$\alpha$ -Ketoglutaric acid forms colourless crystals, m. p. 115—116°; the diethyl ester is a colourless liquid, b. p. 160°/23 mm. The phenylhydrazine of the acid crystallises in almost colourless plates, m. p. 152—153°; on keeping or when heated, the anhydride, 1-phenyl-

5-pyridazinone-3-carboxylic acid,  $\text{NPh}\text{---}\text{C}\begin{matrix} \text{CO} \\ \text{N} \end{matrix}\text{---}\text{CH}_2\text{---}\text{CH}_2$ , is obtained.

It forms colourless plates, m. p. 172°, and the solution in concentrated sulphuric acid is not coloured by either ferric chloride or potassium bichromate.

On the introduction of hydrogen chloride into a warm alcoholic solution of the anhydride, ammonium chloride is eliminated and *ethyl 2-carboxyindole-3-acetate*,  $C_8H_4 \begin{smallmatrix} \text{C}(\text{CH}_2\text{CO}_2\text{Et}) \\ \text{NH} \end{smallmatrix} \text{C}(\text{CO}_2\text{Et})$ , obtained in colourless plates, m. p. 83–84°. E. F. A.

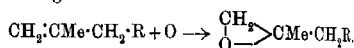
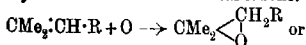
**Oxidation of Unsaturated Compounds with Organic Peroxides. II. Oxidation of Derivatives of Unsaturated Hydrocarbons with One Double Linking.** NIKOLAUS FRILS-CHAEFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 609–620).—It has been already shown that the interaction of hydrocarbons of the series,  $C_nH_{2n-2}$ , and benzoylhydroperoxide proceeds according to the scheme:



vol., i, 255). In the present paper it is shown that the oxidation of derivatives of these hydrocarbons, for example, aldehydes, ketones, alcohols, etc., proceeds in the same way.

Thus, allyl alcohol yields the corresponding oxide (glycide) (compare Nef, Abstr., 1905, i, 3),  $\begin{smallmatrix} O \\ | \\ CH_2 \end{smallmatrix} > CH\cdot CH_2\cdot OH$ .

Oxidation of citronellal (b. p. 103–105°/25 mm.,  $[\alpha]_D + 9.79^\circ$ ,  $D_4^{25} 0.8624$ ) gives *citronellal oxide*,  $C_{10}H_{18}O_2$ , as a colourless liquid, b. p. 126–127°/20 mm.,  $D_4^{20} 0.9437$ ,  $D_4^{25} 0.9344$ ,  $[\alpha]_D + 9.63^\circ$ ,  $n_D^{20} 1.44210$ , which gives all the aldehyde reactions, but does not form a crystalline oxime or semicarbazone. The oxidation proceeds thus:

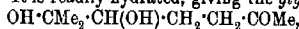


Citronellal oxide readily undergoes hydration to the *glycol*,  $C_{10}H_{20}O_3$ , which is a viscous, colourless liquid, b. p. 180–182°/18 mm., and forms an *acetyl* derivative,  $C_{10}H_{19}O_3Ac$ , b. p. 175–176°/13 mm.,  $D_4^{20} 1.0418$ ,  $D_4^{25} 1.0295$ ,  $n_D^{20} 1.4571$ . From dihydroxydihydrocitronellal dimethylacetal, Harries and Schauwecker (Abstr., 1901, i, 730) also obtained a dihydroxyaldehyde, but the b. p., 158–162°/22 mm., is appreciably lower than that found for the above glycol.

Methylheptenone,  $CMe_2\cdot CH\cdot CH_2\cdot CH_2\cdot COMe$ , on oxidation gives:

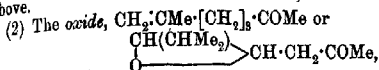
(1) The *oxide*,  $\begin{smallmatrix} CMe_2 \\ | \\ O \end{smallmatrix} > CH\cdot CH_2\cdot CH_2\cdot COMe$ , as a mobile, colourless

liquid, b. p. 68–70°/50 mm., 146.5–147.5°/746 mm.,  $D_4^{20} 0.9870$ ,  $D_4^{25} 0.9718$ ,  $n_D^{25} 1.43031$ ; it is not oxidised by permanganate, reduces Fehling's solution slightly, and does not give a crystalline oxime or semicarbazone. It is readily hydrated, giving the *glycol*,

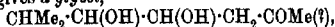


as a mobile liquid, b. p. 139–140°/13 mm.,  $D_4^{20} 1.0698$ ,  $D_4^{25} 1.0582$ ,  $n_D^{25} 1.4610$ , which slowly crystallises; m. p. 65–66°. Dehydration of the glycol yields the *diketone*,  $CHMe_2\cdot CO\cdot CH_2\cdot CH_2\cdot COMe$ , b. p. 117–119°/50 mm., 94–95°/15 mm.,  $D_4^{20} 0.9538$ ,  $D_4^{25} 0.9396$ ,  $n_D^{25} 1.4356$ , which yields a *dioxime*, m. p. 131.5–132°, and a *monosemicarbazone*, m. p. 197–198°. By oxidising methylheptenone with

permanganate, Harries (Abstr., 1902, i, 345) obtained a glycol, and from this a diketone, both having similar properties to the above.



b. p. 115–116°/50 mm.,  $D_4^{20}$  0.9963,  $D_4^{16}$  0.9826,  $n_D^{16.5}$  1.44747. On hydration, it gives a glycol,



b. p. 143–145°/14 mm.,  $D_4^{20}$  1.0700,  $D_4^{16}$  1.0583,  $n_D^{16.2}$  1.4599, m. p. 62–63.5°, which is apparently different from the glycol described under (1). It gives, however, the same diketone on dehydration.

T. H. P.

**Oxidation of Hexoses by Air in Presence of Alkali Hydroxides.** JOSÉ I. DEL ROSARIO (*Revista Filipina Med. Farm.*, 1910, 1, 191).—The oxidation of laevulose by air in presence of alkali hydroxide gives similar products to those obtained by the oxidation of hexoses by Fehling's solution (compare Nef, Abstr., 1898, i, 7; Anderson, Abstr., 1909, i, 881). The oxidation was carried out by bubbling air freed from carbon dioxide through a solution of 100 grams of laevulose in 3500 c.c. of water in which 300 grams of barium hydroxide were dissolved; 1.22 grams of carbon dioxide, 18.3 grams of formic acid, and 77–80 grams of soluble gum were formed. The latter was resolved by Nef's method into glycollic, *d*- and *l*-glyceric, threonic, *d*-mannonic, and *d*-gluconic acids; in addition there was isolated  $\alpha$ -hydroxymethyl-*d*-arabonic acid, which was also obtained by Spoehr (Abstr., 1910, i, 221) on oxidising laevulose with hydrogen peroxide in alkaline solution. No lactic, acetic, or oxalic acid was formed.

W. A. D.

**Acetohalogen-glucoses and *p*-Bromophenylosazones of Maltose and Melibiose.** EMIL FISCHER (*Ber.*, 1911, 44, 1898–1904. Compare Fischer, Abstr., 1910, i, 716).—An optical inversion takes place when anhydrous liquid hydrogen chloride acts on  $\alpha$ -pentacetyldextrose, and  $\beta$ -acetochlorodextrose,  $[\alpha]_D + 160.9^\circ$  in chloroform, is the main product. The conditions for obtaining  $\alpha$ -acetochlorodextrose in this manner have not been again realised (Fischer and Armstrong, Abstr., 1901, i, 257, 671). Similarly, with anhydrous hydrogen bromide,  $\beta$ -acetobromodextrose,  $[\alpha]_D + 199.28^\circ$  in chloroform, is obtained from  $\alpha$ -pentacetyldextrose.  $\beta$ -Acetobromodextrose is conveniently prepared in quantity by the action of anhydrous hydrogen bromide in glacial acetic acid on  $\beta$ -pentacetyldextrose.

The preparation of maltosone from phenylmaltosazone by boiling with benzaldehyde is much facilitated by the presence of 10–15% of benzoic acid in the benzaldehyde.

E. F. A.

**Glucoducose and  $\alpha$ -Glucodecitol.** L. H. PHILIPPE (*Compt. rend.*, 1911, 152, 1774–1776. Compare this vol., i, 12).—Reduction of  $\alpha$ -glucodeconic acid, or of the crude mixture of acid and lactone, leads to the production of  $\alpha$ -glucoducose,  $\text{C}_{10}\text{H}_{20}\text{O}_{16}$ , m. p. 210°; in aqueous

solution it has  $[\alpha]_D^{20} + 37^\circ$ , but after twenty-four hours, or on boiling, shows  $[\alpha]_D^{20} + 50.4^\circ$ . The substance crystallises from water in anhydrous needles, but sometimes separates from concentrated solutions as hexagonal lamellæ containing  $1\text{H}_2\text{O}$ . The hydrated form shows the same rotation as the anhydrous substance. The *phenylhydrazones* crystallises in colourless, prismatic needles, m. p.  $228-229^\circ$ ; the *osazone* in slender, yellow needles, m. p.  $278^\circ$ .

Further treatment of the decose with sodium amalgam converts it into *α-glucodecitol*,  $\text{C}_{10}\text{H}_{22}\text{O}_{10}$ , small, prismatic needles, m. p.  $232^\circ$  (sublimes),  $[\alpha]_D^{20} + 1.2^\circ$ ; the *deca-acetyl* derivative forms rectangular lamellæ, m. p.  $149-150^\circ$ ,  $[\alpha]_D^{20} + 16.0^\circ$  in chloroform solution. It combines with benzaldehyde to form an insoluble *acetal*.

W. O. W.

**The Solubility of Lime in Solutions of Sucrose.** H. CLAASSEN (*Zeitsch. Ver. deut. Zuckerind.*, 1911, 489-509).—To determine the solubility, well-stirred solutions of sucrose were heated with lime at different temperatures for definite intervals of time; the solution was rapidly filtered, and the lime determined in the filtrate, which was also examined polarimetrically.

The solubility of lime in pure solutions of sucrose is independent of the kind of lime when a good commercial sample is used, but it depends on the way in which the lime is added. Most lime dissolves when it is added directly as quicklime, whilst the solubility is the least when an old milk of lime is used. Under the same conditions of experiment the same quantity of lime dissolves.

The solubility increases with the quantity of lime (always in excess) added, until a solubility of 2-2.5% by weight is reached; further increase in the quantity of lime then slightly diminishes the solubility.

Rise in temperature diminishes the solubility, as also does a diminution in the concentration of the sucrose solution. When solutions which have been saturated at  $0^\circ$ ,  $20^\circ$ , or  $50^\circ$  are heated in the presence of excess of lime, part of the lime is deposited as such, and not as calcium sucrate. The amount deposited varies with the conditions, but the amount remaining in solution is always greater than that which would be dissolved by direct addition of the lime at the higher temperature.

On warming the filtrates from solutions which have been saturated at  $0^\circ$  or  $20^\circ$ , a deposit is obtained which contains, not only lime, but also calcium sucrate as a gelatinous precipitate. Filtrates from solutions saturated at  $50^\circ$  give practically no deposit on heating to  $90-100^\circ$ .

If sucrose solutions which have been saturated at a high temperature are cooled in the presence of excess of milk of lime, the latter dissolves until the solubility is the same as that which would have been obtained directly at the lower temperature. With quicklime, however, the solubility is less than that obtained directly, but greater than in the case of milk of lime.

Impure sucrose solutions, such as the thin liquor obtained in the

manufacture of sucrose, behave in the same manner as pure solutions of the same sucrose content. T. S. P.

**Behaviour of Sucrose, and its Decomposition Products on Heating.** J. E. DUSCHSKY (*Zeitsch. Ver. Deut. Zuckerind.*, 1911, 581—608).—As the result of a series of experiments in which the change in the polarisation or in the cupric reducing power was studied, the conclusion is drawn that on heating dextrose either at atmospheric or under increased or reduced pressure, there is no marked increase in the polarisation or reduction in the reducing power. In some cases an increase in the polarisation is observed, indicating the formation of new products; this is due to the use of strong solutions or particularly to the presence of acids, for example, lactic and acetic acids. Lactic acid is particularly active, and in addition prevents the further decomposition of the new products formed. Normally the polarisation first increases on heating, and then decreases as the new products are decomposed. Alkalis have a similar decomposing action, and here in no case was an increase in polarisation observed, very small quantities of alkali being enough to reduce materially the polarisation. Heating of dextrose causes a very small reduction of the reducing power.

Under all pressures levulose is readily decomposed at somewhat low temperatures. A higher temperature has a greater effect than a longer exposure to a lower temperature. A diminution of the pressure protects the levulose to some extent. Less concentrated solutions of levulose are more stable. The products of heating are probably optically inactive and have but a weak reducing power. Lactic and acetic acids protect levulose from decomposition to some extent. E. F. A.

**Yeast-Gum.** HANS VON EULER and ANDOR FODOR (*Zeitsch. physiol. Chem.*, 1911, 72, 339—346. Compare Salkowski, *Abstr.*, 1894, i, 222, 316; Meigen and Spring, 1908, ii, 315).—The gum was prepared by Salkowski's method by means of the copper derivative, and in aqueous solution gave  $[\alpha]_D^{20} + 86.95^\circ$ . The solution, purified by dialysis, does not give precipitates with phosphomolybdic or phosphotungstic acid. When hydrolysed with dilute sulphuric acid, the ratio mannose:dextrose lies between 40:30 and 40:40, the mannose being estimated as its phenylhydrazone. J. J. S.

**Action of Hydriodic Acid on Starch and Dextrin.** WILLIAM OCHSNER DE CONINCK and A. RAYNAUD (*Bull. Soc. chim.*, 1911, [iv], 9, 586—587. Compare this vol., i, 423).—The rate of hydrolysis of starch and dextrin by hydriodic acid is proportional to the concentration of the acid. In both cases complete hydrolysis can be effected, and it is reached more quickly with dextrin than with starch. T. A. H.

**Electrolytic Decomposition of Cellulose.** R. OERTEL (*Chem. Zeit.*, 1911, 35, 713).—By the electrolysis of cellulose in a neutral potassium chloride bath the author has succeeded in transforming

it into a product which is soluble in 10% sodium hydroxide, and is probably a new hydroxycellulose. It can be obtained either by retaining the fibrous structure of cellulose, or in such a form that it gives a milky, colloidal solution with water.

Details are reserved for a future communication.

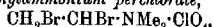
T. S. P.

**Propylamine Peroxide.** EDUARD K. KUBOVSKI and L. NISENMAN (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 654—655).—In the authors' previous paper, the opinion was expressed that salts of pertitanic acid with organic bases (this vol., i, 183) are really compounds of pertitanic acid and peroxides of amines. They have now been able to prepare propylamine peroxide by the action of propylamine on an ethereal solution of hydrogen peroxide at a low temperature. A heavy, viscous liquid separates, and this, on further cooling, forms a white, crystalline mass. This compound is very unstable and was not completely analysed, but the relation between active oxygen and propylamine indicates that it has the formula  $C_3H_7NH_2 \cdot O_2H$ .

T. H. P.

**Perchlorates of the Choline and Neurine Group.** Detection of Choline and Neurine. KARL A. HOFMANN and K. HÖBOLD (*Ber.*, 1911, 44, 1766—1771).—The fact that quaternary ammonium perchlorates are less soluble in water than the perchlorates of primary, secondary, or tertiary amines (*Abstr.*, 1910, i, 818) has been applied to the detection and isolation of choline and neurine. Choline perchlorate itself is too soluble (100 parts of water dissolve 290 parts of the salt at 15°) for this purpose. *Nitratocholine perchlorate*,  $NO_2 \cdot O \cdot CH_2 \cdot CH_2 \cdot NMe_3 \cdot ClO_4$ , m. p. 185—186° (previously described as choline perchlorate, *loc. cit.*), however, answers admirably. It is obtained by evaporating a 0.2% aqueous solution of choline perchlorate with 2 c.c. of 65% nitric acid on the water-bath, dissolving the residue in a little hot water, and adding a few drops of dilute perchloric acid.

*Trimethyldibromoethylammonium perchlorate*,



large, doubly refracting plates (solubility 2.2 at 15°), and *bromovinyl-trimethylammonium perchlorate*,  $CH_2Br \cdot CH \cdot NMe_3 \cdot ClO_4$ , elongated plates (solubility 2.65 at 14°), are about half as soluble as neurine perchlorate (*loc. cit.*).

C. S.

**Molecular State of Organic Ammonium Halides in Non-dissociating Media.** ARTHUR HANTZSCH and O. K. HOFMANN (*Ber.*, 1911, 44, 1776—1783).—Owing to the fact that certain organic ammonium halides have, not only different colours, but also different molecular weights in chloroform (Hantzsch and Leupold, *Abstr.*, 1909, ii, 198), polymerism has been regarded as a cause of difference of colour, and Tinkler has attempted to represent the polymerides of pyridine and acridine methiodides by structural formulae containing tervalent iodine (*Trans.*, 1909, 95, 921). Now the authors are of opinion that these supposed polymerides are really only molecular associations, because (i) the molecular weights of organic ammonium halides, in the same solvent vary with the nature of the anion in

such a way that the chlorides always have the smallest, the iodides the largest, molecular weights, the bromides and thiocyanates showing intermediate values; (ii) one and the same salt in different, non-associating media has a larger or smaller molecular weight according to the greater or smaller associating power of the solvent; (iii) the molecular weight occasionally increases with the concentration in one and the same solvent.

The preceding generalisations have been established by the following experiments. Examined by the ebullioscopic method in dry chloroform, tetrapropylammonium iodide is always quinquemolecular independently of the concentration, tetrapropylammonium chloride is most probably termolecular, whilst triethylammonium chloride is bimolecular and dimethyl- and diethyl-ammonium chlorides are quinquemolecular; the molecular weights of the last three, however, increase with increasing concentration. *iso*Amylammonium chloride does not produce any appreciable rise of the b. p. The degree of association of alkylammonium salts in chloroform does not depend on their molecular weights, but on the amount of the substitution (of the ammonium hydrogen atoms) and the nature of the halogen. The degree of association also depends largely on the solvent; thus, tetra-ethylammonium iodide, which by analogy with tetrapropylammonium iodide should be quinquemolecular in chloroform (actually its solubility is too small for experimental purposes), is almost unimolecular in pyridine.

The molecular weights in chloroform of the 5-phenyl-10-methylacridonium halides given by Hantzsch and Leupold (*loc. cit.*) are too small. The chloride and bromide are bi- to ter-molecular, the thiocyanate is ter- to quadri-molecular, whilst the iodide is constantly quinquemolecular. The simple 5-phenylacridonium halides, however, are only slightly associated in chloroform, whatever the halogen atom. Moreover, 5-phenyl-10-methylacridonium iodide is unimolecular in pyridine or phenol.

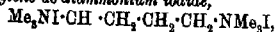
A comparison of the preceding results shows that aliphatic and aromatic ammonium halides of the same degree of substitution are about equally strongly associated in the same solvent.

The chloroform used for ebullioscopic measurements must be absolutely free from alcohol or water. A satisfactory quality can be obtained by shaking commercial chloroform with concentrated sulphuric acid for fifteen minutes, washing thoroughly with dilute sodium carbonate and with water, and drying over ignited potassium carbonate; the purified chloroform should be kept in a full bottle over potassium carbonate, in the dark (see further, this vol., i, 673).

C. S.

[Preparation of Quaternary Ammonium Bases.] FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 231806).—The salts obtained by the exhaustive alkylation of polyacidic bases are converted into quaternary ammonium bases, which are then decomposed by heat.

*Hexamethylbutylene- $\alpha$ - $\delta$ -diammonium iodide,*





on treatment with silver oxide yields the corresponding *hydroxide*, a faintly coloured, strongly basic oil, which is decomposed by heat into erythrene (divinyl) and trimethylamine, whilst  $\beta$ -methylbutylene- $\alpha$ -diamine yields methyldivinyl (isoprene) when treated in a similar manner.

F. M. G. M

**Decomposition of Quaternary Ammonium Hydroxides. I.**  
JULIUS VON BRAUN (*Annalen*, 1911, 382, 1—49).—The thermal decomposition of quaternary ammonium halides is analogous to that of the trialkylammonium bromides (compare Abstr., 1910, i, 189). As a rule, the smallest alkyl group is eliminated in the form of alkyl halide, but exceptions are met with when an olefine linking or a phenyl group is present in the alkyl group, and is adjacent to the nitrogen atom. The following are the common alkyl groups arranged in order of decreasing tendency to be eliminated as alkyl halide: allyl, benzyl, methyl, ethyl, propyl, butyl, amyl, phenyl (compare Collie and Schryver, *Trans.*, 1890, 57, 767; Meyer, this Journ., 1877, ii, 190). Other quaternary ammonium salts, for example, cyanides, thiocyanates, phenoxides, benzoates, and *p*-toluenesulphates, behave in a similar manner. Experiments made with a number of quaternary ammonium hydroxides show that the behaviour is somewhat different; the order of the groups is: allyl, benzyl, ethyl, propyl, *iso*amyl, hexyl, methyl, *isobutyl*, phenyl (compare Collie and Schryver, *loc. cit.*; Claus and Rautenberg, *Abstr.*, 1881, 584; Claus and Hirzel, 1887, 134; Merling, 1891, 1506). The following numbers give the percentage of the hydroxide transformed into methyl alcohol and dimethylalkylamine:  $\text{NMe}_3\cdot\text{Et}\cdot\text{OH}$ , 0%;  $\text{NMe}_3\cdot\text{Pr}\cdot\text{OH}$ , 5—10%;  $\text{C}_2\text{H}_5\cdot\text{NMe}_3\cdot\text{OH}$ , 50%;  $\text{C}_3\text{H}_7\cdot\text{NMe}_3\cdot\text{OH}$ , 60%;  $\text{C}_4\text{H}_9\cdot\text{NMe}_3\cdot\text{OH}$ , 73%;  $\text{C}_5\text{H}_{11}\cdot\text{NMe}_3\cdot\text{OH}$ , 75%;  $\text{C}_6\text{H}_{13}\cdot\text{NMe}_3\cdot\text{OH}$ , 75%; and in each case a decomposition into trimethylamine and an alcohol or olefine also occurs. The following numbers also give the percentage of the hydroxide transformed into methyl alcohol and mixed tertiary base:

$\text{OPh}\cdot[\text{CH}_2]_3\cdot\text{NMe}_3\cdot\text{OH}$ , 10%;  $\text{OPh}\cdot[\text{CH}_2]_4\cdot\text{NMe}_3\cdot\text{OH}$ , 55%;

$\text{OMe}\cdot[\text{CH}_2]_6\cdot\text{NMe}_3\cdot\text{OH}$ , 60%;  $\text{OPh}\cdot[\text{CH}_2]_5\cdot\text{NMe}_3\cdot\text{OH}$ , 60%;

$\text{NH}_2\cdot[\text{CH}_2]_5\cdot\text{NMe}_3\cdot\text{OH}$ , 60%;  $\text{COPh}\cdot\text{NH}\cdot[\text{CH}_2]_5\cdot\text{NMe}_3\cdot\text{OH}$ , 60%.

The amount of olefine tends to diminish, and the amount of corresponding alcohol to increase, with an increase of the molecular weight of the alkyl group present in the trimethylalkylammonium hydroxide, so that trimethylcetylammmonium hydroxide yields practically no cetene. The formation of an olefine or unsaturated compound is regarded as a primary decomposition, and is not attributed to a secondary decomposition of an alcohol. The following numbers are also given:

$\text{CH}_2\text{Ph}\cdot\text{NMe}_3\cdot\text{OH}$ , little;  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NMe}_3\cdot\text{OH}$ , 0%;

$\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{NMe}_3\cdot\text{OH}$ , 70%;  $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_4\cdot\text{NMe}_3\cdot\text{OH}$ , 75%.

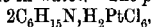
where the number indicates the percentage of the hydroxide decomposed into methyl alcohol and mixed tertiary amine. The general conclusion drawn is, that the manner in which a quaternary ammonium hydroxide decomposes depends first on the tendency of the mobile light groups to be eliminated as alcohols, and, secondly, on the tendency by means of the elimination of water to form olefines of symmetrical

structure. The influence of the second factor is seen by a comparison of the products of decomposition of *n*-heptyl- and *n*-octyl-trimethylammonium hydroxide with the corresponding *cycloheptyl* and *cyclo-octyl* hydroxides (compare Willstätter, Abstr., 1901, i, 223; Willstätter and Waser, 1910, i, 366). Hexenyltrimethylammonium hydroxide (Merling) gives 80% of trimethylamine, owing to the fact that a symmetrical diolefine,  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{:CH}_2\text{:CH}\cdot\text{CH}_2$ , can be formed.

As quaternary ammonium hydroxides are readily prepared, the manner in which they decompose on heating is of importance in connection with the preparation of mixed tertiary amines. The simplest method of preparing butyl-, amyl-, hexyl-, heptyl-, octyl-, and cetyl-dimethylamines and similar compounds is probably by decomposing the corresponding alkyltrimethylammonium hydroxides.

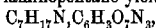
The quaternary ammonium salts can be prepared by the complete methylation of the primary amine, or, in some cases, by the union of trimethylamine with the necessary alkyl iodide or bromide. As a rule, the quaternary hydroxides can be distilled under atmospheric pressure, and the basic products separated from the neutral compounds by means of dilute acid.

*Trimethyl-n-butylammonium iodide*,  $\text{C}_7\text{H}_{15}\text{NI}$ , can be separated from potassium iodide as it dissolves in warm chloroform; it softens at  $225^\circ$ , and has m. p.  $230^\circ$  (decomp.). The corresponding hydroxide is syrupy, and when heated yields dimethylbutylamine,  $\text{NMe}_2\cdot\text{C}_4\text{H}_9$ , as a mobile oil, b. p.  $96^\circ$ , sparingly soluble in water. The *platinichloride*,



crystallises in brilliant, reddish-yellow plates, m. p.  $110^\circ$ , and the *picrate* separates from alcohol in similar plates, m. p.  $98^\circ$ .

Trimethylamylammonium iodide has m. p.  $215^\circ$  (Willstätter and Waser give  $222^\circ$ ), and when decomposed gives  $\Delta^a$ -amylene, but no amyl alcohol.  $\alpha$ -Dimethylaminopentane yields a *picrate*,



which crystallises from alcohol in brilliant, long needles, m. p.  $100^\circ$ . Cyanogen bromide reacts with an ethereal solution of the tertiary base, yielding trimethylamylammonium bromide and *methyl-n-amylcyanamide*,  $\text{C}_6\text{H}_{11}\cdot\text{NMe}\cdot\text{CN}$ . The latter is an oil with a fragrant odour, has b. p.  $109^\circ$ , and when boiled with 30% aqueous alcoholic sulphuric acid yields *methyl-n-amylamine* (Löffler, Abstr., 1910, i, 632; the *picrate* has m. p.  $121^\circ$ , not  $119$ — $120^\circ$ ).

*Trimethylheptylammonium iodide*,  $\text{C}_9\text{H}_{19}\cdot\text{NMe}_3\text{I}$ , prepared from *n*-amylamine (Braun and Sobecki, this vol., i, 128), has m. p.  $167^\circ$ ; the corresponding *hydroxide* is a solid, and when distilled yields  $\Delta^a$ -hexylene, b. p.  $62$ — $63^\circ/740$  mm. and  $D_{20}^{25}$  0.6686. *Dimethyl-n-heptylamine*,  $\text{C}_8\text{H}_{17}\cdot\text{NMe}_2$ , has b. p.  $147^\circ$ ; the *platinichloride* is readily soluble in water and has m. p.  $126$ — $127^\circ$ , and the *picrate* has m. p.  $101^\circ$ . *Trimethyl-n-heptylammonium iodide*,  $\text{C}_{10}\text{H}_{21}\text{NI}$ , forms crystalline plates, which soften at  $143^\circ$  and melt at  $145^\circ$ . The *hydroxide* is a solid, and when distilled yields  $\Delta^a$ -heptylene, heptyl alcohol, and *dimethyl-n-heptylamine*,  $\text{C}_8\text{H}_{17}\text{N}$ . The tertiary base has b. p.  $172^\circ$ , yields a *platinichloride* in the form of felted, reddish-yellow needles, m. p.  $139^\circ$ , and a *picrate*, m. p.  $83^\circ$ . When treated with cyanogen bromide the tertiary base yields *methylheptylcyanamide*,  $\text{C}_7\text{H}_{15}\cdot\text{NMe}\cdot\text{CN}$ , as a

colourless oil with b. p.  $142^{\circ}/15$  mm., and this on hydrolysis with  $33\%$  sulphuric acid gives the secondary base, *methylheptylamine*,  $C_8H_{19}N$ , with b. p.  $168^{\circ}$ . The *picrate* crystallises in yellow needles, m. p.  $97^{\circ}$ , and the *platinichloride* in orange plates, m. p.  $168^{\circ}$ . The *carbamide*,  $C_7H_{15}NMe \cdot CO \cdot NH_2$ , crystallises from a mixture of ether and light petroleum in colourless, glistening plates, m. p.  $100^{\circ}$ .

Trimethyl-*n*-octylammonium iodide, prepared from trimethylamine and *n*-octyl iodide, has m. p.  $138^{\circ}$  (Mugdan, Abstr., 1898, i, 157, gives  $139-141^{\circ}$ ); the *hydroxide* is a solid, and yields a mixture of octylene and octyl alcohol, together with *dimethyl-n-octylamine*,  $C_8H_{17}NMe_2$ , b. p.  $194^{\circ}$ . The *platinichloride* of the tertiary base forms long needles, m. p.  $120^{\circ}$ , and the *picrate* has m. p.  $62-65^{\circ}$ .

*Trimethylcetylammmonium iodide*,  $C_{19}H_{41}NI$ , crystallises in felted needles, m. p.  $222^{\circ}$ , and on treatment with moist silver oxide shows a great tendency to form colloidal silver iodide, and this complicates the preparation of the quaternary hydroxide. The hydroxide when heated does not melt, and yields *dimethylcetylamine*,  $C_{16}H_{33}NMe_2$ , with b. p.  $193-205^{\circ}/18$  mm. The base contains small amounts of non-nitrogenous products, and is best purified by means of the *picrate*,  $C_{18}H_{39}N \cdot C_6H_5O_7N_3$ , which crystallises in long needles, m. p.  $69^{\circ}$ . The pure base has b. p.  $203-205^{\circ}/17$  mm., and its *platinichloride* has m. p.  $83^{\circ}$ , and is practically insoluble in hot water. Cetyl alcohol is also formed during the decomposition of the hydroxide.

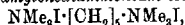
$\gamma$ -*Phenoxypropyltrimethylammonium iodide*,  $OPh \cdot [CH_2]_3 \cdot NMe_3I$ , is best prepared from trimethylamine and  $\gamma$ -phenoxypropyl iodide, and crystallises from alcohol in glistening plates, m. p.  $174^{\circ}$ . The hydroxide on distillation yields trimethylamine and phenyl allyl ether, together with a small amount of phenyl  $\gamma$ -dimethylaminopropyl ether (compare Knorr and Roth, Abstr., 1906, i, 457).  $\delta$ -*Phenoxybutyltrimethylammonium iodide*,  $C_{13}H_{27}ONI$ , is sparingly soluble, and has m. p.  $169^{\circ}$ . When distilled the *hydroxide* yields *phenyl  $\Delta^2$ -butenyl ether*,



b. p.  $208-210^{\circ}$ , together with *phenyl  $\delta$ -dimethylaminobutyl ether*,  $OPh \cdot [CH_2]_4 \cdot NMe_3$ , with b. p.  $139-140^{\circ}/13$  mm. The *platinichloride* is oily, and the *picrate* has m. p.  $108^{\circ}$ .

$\epsilon$ -*Phenoxyamyltrimethylammonium iodide*,  $OPh \cdot [CH_2]_5 \cdot NMe_3I$ , has m. p.  $185^{\circ}$ , and its oily *hydroxide* when distilled yields *phenyl amylene ether* (Braun and Trümpler, Abstr., 1910, i, 26) and *phenyl  $\epsilon$ -dimethylaminoamyl ether*,  $OPh \cdot [CH_2]_5 \cdot NMe_2$ . The latter is a colourless oil with b. p.  $149^{\circ}/11$  mm., and yields a *picrate*, m. p.  $99^{\circ}$ .

Methyl  $\epsilon$ -benzoylaminoamyl ether and phosphorus pentachloride yield benzonitrile and methyl  $\epsilon$ -chloroamyl ether, together with  $\alpha$ -dichloropentane. When a mixture of the two latter compounds is boiled with an alcoholic solution of potassium iodide a mixture of the corresponding iodo-compounds is obtained, and these with trimethylamine yield *hexamethylamylenediammonium iodide*,

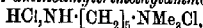


and a small amount of  $\epsilon$ -methoxyamyltrimethylammonium iodide,  $OMe \cdot [CH_2]_5 \cdot NMe_3I$ . The former is sparingly soluble in alcohol, turns brown at  $200^{\circ}$ , and decomposes between  $268^{\circ}$  and  $273^{\circ}$ . The latter dissolves readily in alcohol, and has m. p.  $123-124^{\circ}$ . When

the hydroxide corresponding with the methoxy-salt is distilled, the products are methyl amylenyl ether and *methyl ε-dimethylaminoamyl ether*,  $\text{OMe} \cdot [\text{CH}_2]_5 \cdot \text{NMe}_2$ .

*ε-Benzoylaminoamyltrimethylammonium hydroxide* (Abstr., 1910, i, 820) has to be decomposed under reduced pressure, and gives a 60% yield of benzoyldimethylamylenediamine and a 40% yield of pentenylbenzamide.

The *hydrochloride of aminoamyltrimethylammonium chloride*,

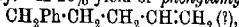


obtained by hydrolysing the corresponding benzoyl derivative with concentrated hydrochloric acid at  $160^\circ$ , forms hygroscopic crystals, and the *platinichloride* forms red crystals, m. p.  $218^\circ$ . To obtain the hydroxide, the chloride is transformed into the sulphate by means of silver sulphate, and this is then decomposed with barium hydroxide solution. *Aminoamyltrimethylammonium hydroxide* is a sticky mass, and when distilled under atmospheric pressure yields *α*-dimethylcadaverine and methyl alcohol, together with trimethylamine, water, and *Δ<sup>5</sup>-pentenylamine*. The unsaturated amine is a colourless oil with an intense odour, has b. p.  $91-94^\circ$ , absorbs water and carbon dioxide, and yields a *platinichloride*,  $\text{C}_{10}\text{H}_{24}\text{N}_2\text{PtCl}_6$ , in the form of red plates, m. p.  $166^\circ$  (decomp.). The *aurichloride* sinters at  $180^\circ$  and has m. p.  $135^\circ$ , and the *benzenesulphonyl* derivative is oily and readily soluble in alkalis. The quaternary salt, *trimethylpentenylammonium iodide*,  $\text{C}_5\text{H}_9\text{NMe}_3\text{I}$ , has m. p.  $195^\circ$ .

*β-Phenylethyltrimethylammonium bromide* (this vol., i, 35) is readily prepared from *β*-phenylethyl bromide and trimethylamine, and the corresponding hydroxide decomposes into trimethylamine and styrene when its aqueous solution is heated on the water-bath (compare Freund, Abstr., 1899, i, 308; Pschorr, 1904, i, 767; 1905, i, 590).

*γ-Phenylpropyltrimethylammonium hydroxide* (compare Tafel and Senter, Abstr., 1894, i, 579) is more stable, and is decomposed when strongly heated, giving a 70% yield of phenylpropyldimethylamine, b. p.  $225^\circ$ , and a 28% yield of propenylbenzene, b. p.  $169-171^\circ$ .

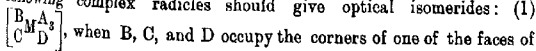
*ε-Phenylamyltrimethylammonium hydroxide* (Abstr., 1910, i, 844) gives a 75% yield of *ε-phenylamylidimethylamine*,  $\text{CH}_3\text{Ph} \cdot [\text{CH}_2]_5 \cdot \text{NMe}_2$ , as a colourless liquid with b. p.  $134-135^\circ$ ; its *picrate* and *platinichloride* are both oily. A 20% yield of *phenylamylene*,



is also formed. It is a colourless liquid with b. p.  $197-198^\circ$ ,  $D_4^{20}$  0.8851, and  $n_D^{20}$  1.5064. The position of the olefine linking has not been settled.

J. J. S.

The *Asymmetric Cobalt Atom*. I. ALFRED WERNER [with V. L. KING and E. SCHOLZE] (*Ber.*, 1911, 44, 1887-1898).—According to the author's co-ordination theory, compounds containing the following complex radicles should give optical isomerides: (1)



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an octahedron. (2)  $\left[ \begin{smallmatrix} A & C_2 \\ B & D_2 \end{smallmatrix} M \right]$ , when the groups combined with the metal atom, M, take up the following positions:

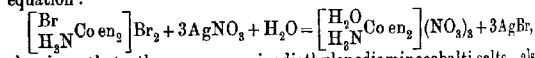


In the second case it is not necessary for the groups C and D to be different, and one of the simplest cases would be when the groups CC and DD are replaced by ethylenediamine, giving compounds of the type  $\left[ \begin{smallmatrix} A & en_2 \\ B & \end{smallmatrix} M \right]$ . When the groups A and B are in the *cis*-position, the two optical isomerides would be represented by the space formulae:



The compounds 1-chloro-2-amminediethylenediaminecobalt salts,  $\left[ \begin{smallmatrix} Cl \\ H_3N \\ H_2N \end{smallmatrix} Co en_2 \right] X_2$ , and 1-bromo-2-ammine-diethylenediaminecobalt salts,  $\left[ \begin{smallmatrix} Br \\ H_3N \\ H_2N \end{smallmatrix} Co en_2 \right] X_2$ , have been prepared and resolved into their optically-active isomerides by means of *d*-bromocamphorsulphonic acid. The salts of the bromo-ammine series are the more easily resolved, because of the great difference in solubility between the isomeric *d*-bromocamphorsulphonates. In both series the *d*-bromocamphorsulphonate of the *d*-isomeride is the more sparingly soluble.

The active compounds are very stable. The aqueous solutions of the bromides of the bromo-ammine series can be kept for a long time at the ordinary temperature, or even heated just to boiling without undergoing racemisation. The activity is also maintained when the bromine atom in the complex is taken out with silver nitrate, according to the equation:



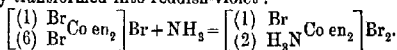
showing that the aquo-amminediethylenediaminecobalt-salts also give optical isomerides. No racemisation takes place when various salts are formed in the two series, as will be seen in the experimental part.

The fact that such active compounds have been prepared shows that the distinction between valency compounds and molecular compounds can be maintained no longer.

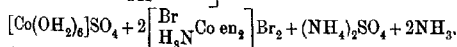
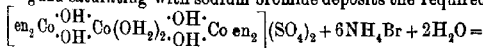
*Optically-active Chloro-amminediethylenediaminecobalt-salts,  $YX_2$* , where  $Y = \left[ \begin{smallmatrix} Cl \\ H_3N \\ H_2N \end{smallmatrix} Co en_2 \right]$ .—The starting point for the preparation of these salts was the racemic compound 1-chloro-2-amminediethylenediaminecobalt-chloride,  $\left[ \begin{smallmatrix} (1) & Cl \\ (2) & H_3N \end{smallmatrix} Co en_2 \right] Cl_2$ , which was prepared by

tritulating acid-free 1 : 6-dichlorodiethylenediaminecobalti-chloride with concentrated ammonia. The green salt first dissolves and then the solution sets to a mass of red crystals of the required salt. Forty grams of this salt were dissolved in 250 c.c. of water, and a solution of 115 grams of silver *d*-bromocamphorsulphonate in 350 c.c. of water added. After collecting the silver bromide, the filtrate, on keeping, deposits short, slender, red prisms. These are collected as soon as felted, silky needles begin to form alongside them, and the filtrate, after four to six hours, solidifies to a mass of these needles. The former compound consists of *d*-1-chloro-2-amminediethylenediaminecobalti-*d*-bromocamphorsulphonate,  $\text{Y}(\text{O}_3\text{S}\cdot\text{O}\cdot\text{C}_{10}\text{H}_{14}\text{Br})_2$ , and after recrystallisation from water forms flat, slender, prismatic crystals;  $[\alpha]_D = +69.5^\circ$  and  $[\text{M}]_D = +592.14^\circ$ . The latter compound is 1-1-chloro-2-amminediethylenediaminecobalti-*d*-bromocamphorsulphonate, and forms bluish-red, long, slender needles, with  $[\alpha]_D = +31.25^\circ$  and  $[\text{M}]_D = +362.1^\circ$ . The *d*-bromide,  $\text{YBr}_2$ , was prepared from the bromocamphorsulphonate either by direct treatment with concentrated hydrobromic acid, or else by forming the sparingly soluble *dithionate*, and tritulating that compound with concentrated hydrobromic acid. It forms cherry-red, small, leaf-like crystals, which have  $[\alpha]_D = +43.1^\circ$  and  $[\text{M}]_D = +172.34^\circ$ . The rotatory power was unchanged when the bromide was again obtained after being transformed successively into the dithionate, bromide, platinichloride, nitrate and bromide, neither did heating the solution to  $70^\circ$  alter the rotation. The 1-bromide was obtained in the same way as the *d*-bromide, and corresponded completely with the latter in colour, shape of crystals, and solubility;  $[\alpha]_D = -43.1^\circ$  and  $[\text{M}]_D = -168.43^\circ$ .

*Optically active 1-bromo-2-amminediethylenediaminecobalti-salts*,  $\text{YX}_2$ , where  $\text{Y} = \left[ \begin{smallmatrix} \text{Br} \\ \text{H}_3\text{N} \end{smallmatrix} \text{Co en}_2 \right]$ , were prepared from 1 : 2-bromoamine-diethylenediaminecobalti-bromide,  $\left[ \begin{smallmatrix} (1) \text{ Br} \\ (2) \text{ H}_3\text{N} \end{smallmatrix} \text{Co en}_2 \right] \text{Br}_2$ . This salt was obtained according to the following two methods: (1) 1 : 6-Dibromodiethylenediaminecobalti-bromide is moistened with water and treated with 1 : 1 ammonia at a low temperature until the green salt is completely transformed into reddish-violet:



(2) Ten grams of tetraethylenediaminediaquotetrolidicobalticosulphate and 30 grams of ammonium bromide are covered with water and the mixture heated. A reddish-violet solution results, which on cooling and saturating with sodium bromide deposits the required salt:



The resolution of this salt by means of the *d*-bromocamphorsulphonate was carried out in a manner similar to that described for the chloroamine salt. The *d*-1-bromo-2-amminediethylenediaminecobalti-*d*-bromocamphorsulphonate,  $\text{Y}(\text{O}_3\text{S}\cdot\text{O}\cdot\text{C}_{10}\text{H}_{14}\text{Br})_2$ , crystallises out first in the form of dark, thick, long, reddish-violet needles;  $[\alpha]_D = +65.7^\circ$  and

$[M]_c = +588.7^\circ$ . The addition of sodium dithionate to the mother liquors gives a precipitate of a racemic dithionate; this is collected, and further addition of sodium dithionate to the filtrate produces, on standing, a deposit of the active dithionate, which serves as the starting point for salts of the *l*-series.

The *d*-chloride,  $YCl_2$ , was obtained from the *d*-bromocamphor-sulphonate by treatment with concentrated hydrochloric acid. It forms dark reddish-violet, shining, flat crystals, and has  $[a]_c = +50.6^\circ$  and  $[M]_c = +175.6^\circ$ . The solution shows no signs of racemisation after keeping for six days. The *d*-bromide,  $YBr_2$ , was obtained similarly, using hydrobromic acid, and forms small, shining, dark violet needles;  $[a]_c = +46.25^\circ$  and  $[M]_c = +201.65^\circ$ . The 0.8% aqueous solution was not racemised when heated for a short time at the boiling point. The *d*-nitrate,  $Y(NO_3)_2 \cdot H_2O$ , prepared from the bromocamphor-sulphonate and fuming nitric acid, forms dark violet columns. It loses  $1H_2O$  at  $100^\circ$ , and has  $[a]_c = +45.0^\circ$  and  $[M]_c = +188^\circ$ .

The *l*-bromide,  $YBr_2$ , was obtained as dark reddish-violet, needle-shaped crystals by treating the *l*-dithionate with concentrated hydrobromic acid. It has  $[a]_c = -45^\circ$  and  $[M]_c = -196.2^\circ$ . T. S. P.

**Oxidation of the Amino-acids. I. Glycine and Cystine.** W. DENIS (*J. Biol. Chem.*, 1911, 9, 365—374).—Glycine on complete oxidation with alkaline potassium permanganate yielded oxalic acid, carbon dioxide, ammonia, and nitric acid. If the oxidation was incomplete, traces of formic and glyoxylic acids could be detected. A modification of the existing methods for the preparation of cystine is described; on complete oxidation it yields sulphuric, oxalic, acetic, and nitric acids, carbon dioxide, ammonia, and free sulphur; if the oxidation was incomplete, traces of pyruvic acid were found.

W. D. H.

**Action of isoButylamine and Di-isoButylamine on  $\alpha$ -Bromobutyric Acid.** JEAN NIVIÈRE (*Compt. rend.*, 1911, 152, 1673—1674).— $\alpha$ -Hydroxybutyric acid is the only product when di-isoButylamine acts on  $\alpha$ -bromobutyric acid. isoButylamine reacts, forming isoButylamine  $\alpha$ -isobutylaminobutyrate.  $\alpha$ -isoButylaminobutyric acid,  $C_4H_9 \cdot NH \cdot CHEt \cdot CO_2H$ , occurs in pearly lamellae, which sublime and decompose without melting. Heated in hydrogen chloride at  $180$ — $200^\circ$  it does not form a piperazine derivative, but loses carbon dioxide, yielding the corresponding secondary amine. The amino-acid forms a hydrochloride, crystallising with  $1.5H_2O$ , a platinichloride crystallising in red needles with  $2H_2O$ , decomp.  $100$ — $110^\circ$ , an aurichloride, a picrate, and copper and silver salts. The hydrochloride, platinichloride, and picrate of the ethyl ester are uncrystallisable.

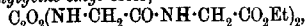
W. O. W.

**Action of Oxalyl Chloride on Amines and Amides.** J. TH. BORNWATER (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 42—45).—Oxalyl chloride in ethereal solution at the ordinary temperature gives with piperidine, oxalylpiperidide; with aniline, oxanilide, and with *o*- and *m*-nitranilines, the corresponding dianilides. With 2:4-dinitroaniline in boiling benzene, oxalyl-di-2:4-dinitroanilide resulted.

Oxalyl chloride reacts *directly* in boiling benzene with the hydrochlorides of the amines, such as aniline and piperidine, also with those of the amino-acid esters. Of the latter, the following compounds have been prepared:

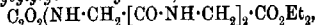
*Oxalyl diglycine ethyl ester*,  $C_2O_2(NH \cdot CH_2 \cdot CO_2Et)_2$ , m. p. 143°.

*Oxalyl diglycylglycine ethyl ester*,



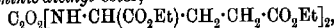
lustrous leaflets, giving the biuret reaction, m. p. 250°.

*Oxalyl di-diglycylglycine ethyl ester*,



forming silky needles, giving a reddish-violet biuret reaction, m. p. 302°.

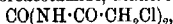
As an example of the amino-derivatives of dibasic acids, the hydrochloride of the diethyl ester of glutamic acid was found to give *oxalyl di-glutaminic diethyl ester*,



m. p. 94.5°.

The author suggests the possibility of obtaining similar oxalyl compounds from polypeptides in general, and of the ultimate synthesis of the proteins, which, as shown by Schützenberger many years ago, all yield oxalic acid by resolution with barium hydroxide.

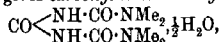
With simple amides, oxalyl chloride yields in some cases carbonyl and not oxalyl derivatives. For example, with benzamide, di-benzoyl-carbamide, and with chloroacetamide, *dichloroacetylcarbamide*,



white needles, m. p. 171°, is produced, but benzanilide gives *oxalyl di-benzanilide*,  $C_2O_2(NPh \cdot CPh)_2$ , m. p. 210°.

Ethyl urethane yields carbonyl diethylurethane, but methylethyl urethane gives *oxalyl dimethylethylurethane*,  $C_2O_2(NMe \cdot CO_2Et)_2$ , m. p. 87°. Carbamide gives, in ether at the ordinary temperature, parabanic acid and, apparently *oxalyl diureide*,  $C_2O_2(NH \cdot CO \cdot NH_2)_2$ , which is quite different from Grimaux's compound (Abstr., 1880, 105) wrongly termed oxalyl diureide in German literature. It is quite insoluble in the ordinary solvents, and gives no biuret reaction.

†Dimethylcarbamide gives cholestrophan, but *as*-dimethylcarbamide (in boiling benzene) gives *carbonyl di-as-dimethylcarbamide*,



in beautiful prisms, m. p. 140°.

J. D. K.

**Iodogorgonic Acid.** MARTIN HENZE (*Zeitsch. physiol. Chem.*, 1911, 72, 505—506).—Polemical. A point of priority, Wheeler and Jamieson having claimed that they and not the author were the first to describe di-iodotyrosine as a decomposition product of iodogorgonic acid.  
W. D. H.

**Reduction of Potassium Cyanate with Hydrogen.** A. P. LUOFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 650—651).—When dry hydrogen is passed through a tube heated at 400° in an electric furnace and containing a platinum boat filled with potassium cyanate, the latter undergoes reduction to the cyanide. The reaction is



apparently complicated by secondary reactions, since the loss in weight of the cyanate often exceeds the increase in weight of a calcium chloride tube situate at the far end of the tube.

T. H. P.

**Formation of Cyanates from Nitrites.** A. P. LIDOFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 651—652).—If a mixture of sodium nitrite (5 grams) with 3—5 times the calculated quantity of finely divided carbon (5 grams) is introduced, in small portions, into a heated platinum dish or crucible, energetic reduction of the nitrite occurs, an aqueous solution of the fused mass no longer developing nitric oxide when shaken with mercury and sulphuric acid. The products formed are cyanate, a small proportion of cyanide and sodium carbonate, together with other cyanogen compounds of an acid character. One of the latter forms a barium salt which is soluble in a neutral solution, but is immediately deposited in shining scales on addition of a small quantity of potassium hydroxide; when freshly prepared, this salt does not give any evolution of gas when treated with acid, but it darkens later and then yields with acids, "carbon acid" gas, the weight of which is rather less than that of carbon dioxide.

T. H. P.

**Oxidation of Sodium Cyanamide and Cyanates with Hydrogen Peroxide and Alkaline Bromine Solution.** A. P. LIDOFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 652—653).—By the interaction of sodium cyanamide solution and a solution of bromine in sodium hydroxide, free from carbon dioxide, in a nitrometer, only about 15—25% of the nitrogen is evolved. Decomposition of the alkaline solution with phosphoric acid results in the development of "carbon acid" gas with a small admixture of hydrogen bromide.

A 5% solution of sodium cyanamide was oxidised by hydrogen peroxide, the latter being added first in the cold and finally on boiling until the solution, which originally gave a yellow precipitate of lead cyanamide with lead acetate, gave a pure white precipitate. On boiling the liquid, a distinct smell of ammonia was observed. To the cooled liquid, lead acetate was added as long as a precipitate was formed, this being then washed with water, alcohol and ether. The lead salt weighed 12 grams, and the gas evolved with potassium hydroxide, 1.902 grams.

When potassium cyanate and an alkaline solution of bromine are allowed to react and barium chloride is added to the liquid, a precipitate is obtained which, with phosphoric acid, gives a quantity of "carbon acid" gas, 1.872—1.915, corresponding closely with that obtained from the cyanamide; similar results are obtained when the oxidation is effected by hydrogen peroxide.

The conclusion is drawn that, under the above conditions, the cyanogen group undergoes oxidation to oxycyanogen, CNO.

T. H. P.

**Constitution of Prussian Blue.** ARNALDO BRIONI (*Boll. Chim. Farm.*, 1911, 50, 165—169).—Polemical. The author furnishes arguments and experimental evidence against the view put forward by

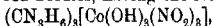
Tarugi and Ravello (*Atti VI Congr. Chim. appl.*, 1906) that Prussian blue is to be regarded as a ferrous or ferrous potassium salt of an oxyferrohydrocyanic acid.

R. V. S.

**Cobaltinitrites.** ARTHUR ROSENHEIM and ABRAHAM GARFUNKEL (*Ber.*, 1911, 44, 1865—1873).—The authors show that the complex cobaltinitrites previously investigated by Rosenheim and Koppel (*Abstr.*, 1898, ii, 430), and salts of a cobalt-3-hydroxo-3-nitrite anion studied by Hofmann and Buchner (*Abstr.*, 1909, i, 775) belong to the same class. Two cobalt-3-guanidinium-3-hydroxo-3-nitrites have also been obtained, these probably being isomerides, as predicted by Werner's theory, and the first of their kind. Furthermore, a new class of compounds, the cobalt-2-acetylacetonato-2-nitrites, has been prepared.

**Cobalt-3-hydroxo-3-nitrites.**—When a concentrated solution of cobalt-3-sodium-6-nitrite,  $\text{Na}_3\text{Co}(\text{NO}_2)_6$ , to which an equimolecular proportion of guanidine carbonate has been added, is evaporated over sulphuric acid, amber-coloured, tabular crystals are obtained, having the composition  $(\text{CN}_3\text{H}_3)_2\text{Na}[\text{Co}(\text{NO}_2)_3]$ , which show all the reactions of the cobalt-6-nitrites. When 3 mols. of guanidine carbonate are used to 1 mol. of the cobaltinitrite, a deep red solution results, from which garnet-red, shining crystals, having the composition  $(\text{CN}_3\text{H}_3)_3[\text{Co}(\text{OH})_3(\text{NO}_2)_3]$ , are obtained. They agree, in all their properties, with the crystals described by Hofmann and Buchner as having the composition  $(\text{CN}_3\text{H}_3)_2\text{Na}[\text{Co}(\text{OH})_3(\text{NO}_2)_3]$ , but do not contain sodium.

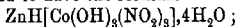
The mother liquors from the garnet-red crystals give a further deposit of dark brick-red needles, having the formula



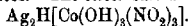
and agreeing in properties and composition with the compound previously obtained by Hofmann and Buchner.

The two compounds of the same composition (garnet-red crystals = A; brick-red = B) differ in appearance, solubility, and some precipitation reactions. With a solution of thallous nitrate, A gives immediately a microcrystalline, cinnabar-red precipitate, having the composition  $\text{Tl}_3\text{H}[\text{Co}(\text{OH})_3(\text{NO}_2)_3]$ , whereas B, after a few minutes, deposits brownish-red crystals of the formula  $\text{Tl}_2(\text{CN}_3\text{H}_3)[\text{Co}(\text{OH})_3(\text{NO}_2)_3]$ .

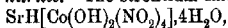
The zinc salt, previously prepared by Rosenheim and Koppel (*loc. cit.*), is now found to have the formula



with thallous nitrate the solution deposits the above-mentioned cinnabar-red thallium salt, proving that the zinc salt belongs to the cobalt-3-hydroxo-3-nitrites. The silver salt has the formula



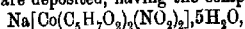
**Cobalt-2-hydroxo-4-nitrites.**—The strontium salt,



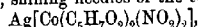
is the only one which has been obtained pure. It is prepared by leading nitrous gases into a cooled suspension of cobalt carbonate and strontium carbonate, and forms small, garnet-red prisms, which are unstable as such, and in solution, nitrous acid being liberated.

**Cobalt-2-acetylacetonato-2-nitrites.**—When concentrated solutions of

sodium acetylacetonate and sodium cobaltinitrite are mixed and kept, purple-red crystals are deposited, having the composition



which lose  $5\text{H}_2\text{O}$  in a vacuum over sulphuric acid. The anhydrous salt is also obtained as slender, bright-red needles, when the solution crystallises at  $30^\circ$ . The aqueous solution gives characteristic precipitates with salts of the alkali metals, of thallium and of silver. The *potassium* salt,  $\text{K}[\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{NO}_2)_2] \cdot \text{H}_2\text{O}$ , forms hair-like, light brownish-red needles; the *ammonium*, *caesium*, and *rubidium* salts are similar in appearance to the potassium salt. The *thallium* salt,  $\text{Tl}[\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{NO}_2)_2]$ , forms a microcrystalline, brownish-yellow precipitate. Dilute solutions of the sodium salt give, with silver nitrate, reddish-brown, shining needles of the composition



whereas a saturated solution gives a dark yellow precipitate of the composition  $\text{Ag}_2[\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{NO}_2)_2]$ .

A solution of the sodium salt, on being boiled, deposits deep green crystals, together with brown, flocculent decomposition products. The crystals are soluble in ether, and consist of cobaltacetylacetonate,  $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_3$ . When sodium acetylacetonate is added to the mother liquors from which the salt  $\text{Na}[\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{NO}_2)_2]$  has crystallised, bright red, hair-like needles having the composition  $\text{Na}[\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2]$  are obtained. This compound gives the colour reaction of acetylacetone with ferric chloride, whereas the complex cobalt-2-acetylacetonato-2-nitrites do not.

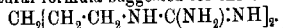
Other 1:3-diketones, such as benzoylacetone, as also acetoacetic ester, give compounds analogous to those obtained with acetylacetone.

*Zinc* and *cadmium acetylacetonates*,  $\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2$  and  $\text{Cd}(\text{C}_5\text{H}_7\text{O}_2)_2$ , were obtained as white needles by the action of sodium acetylacetonate on zinc and cadmium sulphates respectively.

T. S. P.

**Synthesis of Pentamethylenediguandine.** OTTO RIPEA (*Zeitsch. physiol. Chem.*, 1911, 72, 484—485).—When an aqueous solution of pentamethylenediamine is left in contact with a large excess of cyanamide for seventeen days in a desiccator at the ordinary temperature, the solution then treated with sulphuric acid and silver sulphate, then neutralised with barium hydroxide and filtered, and the filtrate saturated with barium hydroxide, a precipitate is obtained, which, after treatment with sulphuric acid and hydrogen sulphide, yields pentamethylenediguandine sulphate. This forms well developed crystals, sparingly soluble in water, and is not molten at  $300^\circ$ .

The *aurichloride*,  $\text{C}_7\text{H}_{18}\text{N}_6 \cdot 2\text{HAuCl}_4$ , crystallises well, and has m. p.  $161^\circ$ . The structural formula suggested for the base is



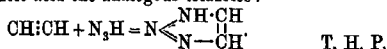
The reaction between cyanamide and pentamethylenediamine is quite different from that between cyanamide and tetramethylenediamine (Kossel, *Abstr.*, 1910, i, 655).

J. J. S.

**Relations between Certain Derivatives of Oxygen and of Nitrogen.** ANGELO ANGELI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 625—627. Compare *Abstr.*, 1910, ii, 844, 948).—Harriss (*Abstr.*,

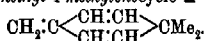
1910, i, 607) has shown that the action of ozone on an oxime results in the formation of an ozonide, which has a ring structure, and which can be resolved into a ketone and nitric acid. The latter contains the grouping  $\text{O}\cdot\text{N}(\text{OH})\cdot\text{O}$  in place of the  $\text{O}\cdot\text{O}\cdot\text{O}$  grouping of the ozone. Nitric acid can further be transformed into the amino-compound,  $\text{O}\cdot\text{N}(\text{NH}_2)\cdot\text{O}$ , which readily loses a molecule of water, giving nitrous oxide,  $\text{N}\cdot\text{N}\cdot\text{O}$ , two of the oxygen atoms of ozone now having been replaced by nitrogen atoms. Then, by the action of ammonia in the form of its sodium derivative, nitrous oxide is converted into hydrazoic acid, the total change from ozone being:  $\text{O}\cdot\text{O}\cdot\text{O} \rightarrow \text{N}\cdot\text{N}\cdot\text{NH}$ . These

two extreme terms of this series of changes exhibit considerable similarity. Thus, they are both formed with absorption of heat and are explosive, and both are poisonous and have suffocating odours. Both react with compounds having multiple linkings, ozone forming ozonides and hydrazoic acid the analogous triazoles:



**Hydroaromatic Compounds.** Hydrocarbon,  $\text{C}_9\text{H}_{10}$ , of the Semibenzene Series. KARL AUWERS and KARL MÜLLER (*Ber.*, 1911, 44, 1595—1608).—The previously described semibenzene derivatives all contain chlorine, whilst hydroaromatic ketones unite with hydrogen and form phenols with the elimination of methylene chloride when attempts are made to prepare semibenzene derivatives from them. The alcohols obtained from these ketones by the Grignard reaction behave differently.

The alcohol,  $\text{OH}\cdot\text{CMe}\cdot\begin{array}{c} \text{CH}:\text{CH} \\ \diagup \quad \diagdown \\ \text{CH}:\text{CH} \end{array}\cdot\text{CMe}\cdot\text{CHCl}_2$ , is converted on treatment with sodium and moist ether into 1:1:4-trimethylcyclo- $\Delta^{2,3}$ -hexadiene-4-ol, although the yield is unsatisfactory, and this is readily converted into 1:1-dimethyl-4-methylenecyclo- $\Delta^{2,3}$ -hexadiene,



The alcohol, trimethylcyclohexadienol, crystallises in colourless, lustrous needles, m. p.  $43^\circ\text{--}44^\circ$ , b. p.  $169^\circ\text{--}170^\circ/760\text{ mm.}$ , and is characterised by the fact that when pure it distils without decomposition. On the other hand, it is very sensitive to acids, and even pure preparations decompose slowly on keeping. Strong and weak acids and acid salts all bring about the decomposition to the hydrocarbon, which, being insoluble in water, has its presence made evident by the aqueous solution of the alcohol becoming cloudy.

The physical constants of the new hydrocarbon are compared with those of the isomeric benzene derivatives mesitylene,  $\psi$ -cumene and  $p$ -methylethylbenzene. Owing to the ease with which it undergoes polymerisation or rearrangement, the purification is a matter of great difficulty; it is best accomplished by rapid distillation in steam under reduced pressure.

The hydroaromatic hydrocarbon has a lower density,  $D_4^{20}$  0.839, than its aromatic isomerides. Spectrochemically the high exaltation of

the specific refractive and dispersive powers of the hydrocarbon is of interest.

Unlike the chlorinated semibenzene, the hydrocarbon is only slowly changed by heat even at  $160^{\circ}$ , and the products are mainly condensation products,  $D_4^{20}$  0.8837,  $n_D^{20}$  1.51209.

Aromatic products were obtained by distilling the methylene derivative in hydrogen under reduced pressure, amongst which  $\psi$ -cumene was identified. It is undecided whether this is formed during distillation or at the time of decomposition of the hydroaromatic alcohol. The methylene derivative is immediately oxidised in the cold by potassium permanganate; it unites with bromine, but a mixture of products is formed. Several hydrocarbons are formed on reduction with sodium and moist ether.

E. F. A.

**Old and New Benzene Formulæ.** ISRAEL LIFSCHITZ (*Zeitsch. angew. Chem.*, 1911, 24, 1153—1161).—An account of the various structural formulæ which have been put forward for the benzene molecule. The author favours Werner's formula, but considers that it will be possible to combine it with that of Stark in such a way that all the various reactions and phenomena can be accounted for.

T. S. P.

**Bromination of cycloHexane.** F. BODROUX and FELIX TABOURT (*Bull. Soc. chim.*, 1911, [iv], 9, 592—594. Compare Markownikoff, *Abstr.*, 1898, i, 637).—In diffused sunlight bromine acts extremely slowly on cyclohexane at its boiling point, but in direct sunlight the boiling hydrocarbon decolorises bromine rapidly, forming cyclohexyl bromide and some polybromo-derivatives. In quartz vessels and exposed to ultra-violet rays from a mercury lamp, the hydrocarbon does not react with bromine. cycloHexyl bromide at the boiling point,  $163^{\circ}$ , reacts with bromine, forming some dibromocyclohexane, b. p.  $144-145^{\circ}$ /100 mm., which is probably the 1:2-isomeride.

T. A. H.

**Additive Compounds of *m*-Dinitrobenzene.** PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 46—47).—A solution of *m*-dinitrobenzene in aniline deposits on cooling red crystals, m. p.  $41-42^{\circ}$ , losing aniline on exposure to air. Similarly, dimethyl-*p*-toluidine yields a black, unstable compound, m. p.  $43^{\circ}$ . With  $\alpha$ -naphthylamine in alcoholic solution are produced red needles, m. p.  $57^{\circ}$ . Similarly, dimethyl- $\beta$ -naphthylamine gives dark red needles, m. p.  $52-53^{\circ}$ . Tetramethyl-*m*-phenylenediamine yields a very dark garnet-red substance, m. p.  $58^{\circ}$ . With benzidine are obtained black crystals, m. p.  $128^{\circ}$ , decomposed by hydrochloric acid. All the foregoing compounds contain an equal number of molecules of amine and dinitrobenzene.

4:4'-Tetramethyldiaminodiphenylmethane gives garnet-red plates or crystals, m. p.  $76^{\circ}$ , containing 2 mols. of amine per mol. of dinitrobenzene.

4:4'-Tetramethyldiamidobenzophenone in alcoholic solution gives red plates, m. p.  $91^{\circ}$ , containing 2 mols. of dinitrobenzene per mol. of the base.

J. D. K.

**Indene Series.** RUDOLF WEISSGERBER (*Ber.*, 1911, 44, 1436—1448). [With F. KRAFT.]—1-Alkyl derivatives of indene (compare Marckwald, *Abstr.*, 1900, i, 434) can be prepared by the action of alkyl halides on sodioindene (*Abstr.*, 1909, i, 219). As a rule, not readily volatile tarry products are also formed. With benzyl chloride and toluene a 30% yield of 1-benzylindene is obtained. It has b. p. 185°/18 mm., and crystallises from alcohol in yellow prisms, m. p. 33—34°.

[With P. BREHME.]—*Di-indene*,  $C_{18}H_{16}$ , can be obtained by boiling indene for ten to twenty-four hours with its own weight of glacial acetic acid; it has b. p. 235—245°/16 mm., and crystallises from glacial acetic acid in nodular masses, m. p. 51°. It is stable towards oxidising agents, and a quantitative yield can also be obtained by boiling indene for fifteen hours with syrupy phosphoric acid.

[With M. VOGEL, A. DOMBROWSKY, and F. KRAFT.]—A 75% yield of indene-1-carboxylic acid,  $CH \begin{smallmatrix} \diagup C_6H_5 \\ \diagdown CH \end{smallmatrix} > CH \cdot CO_2H$ , is obtained by passing dry carbon dioxide into the fused sodium indene from heavy benzene, and a theoretical yield by passing carbon dioxide into a xylene suspension of the finely divided sodioindene. It crystallises from toluene in needles, m. p. 156—157°, has b. p. 193—195°/12 mm. (compare Grignard and Courtot, this vol., i, 538), and differs entirely from the acid described by Perkin and Révay (*Trans.*, 1894, 65, 238). It combines with bromine slowly, and the additive compound has m. p. 136—137° (decomp.). The methyl ester,  $C_{11}H_{10}O_2$ , is a pale yellow oil, b. p. 153—154°/23 mm., with a fragrant odour; the ethyl ester has b. p. 164°/24 mm. When heated for several hours at 180° in an oil-bath, the acid yields *di-indenedicarboxylic acid*,  $C_{20}H_{18}O_4$ , which crystallises from boiling glacial acetic acid in compact needles, m. p. 265° (decomp.).

[With P. BREHME.]—Chlorohydroxyhydrindene (Spilker, *Abstr.*, 1893, i, 519) is readily obtained by the addition of hypochlorous acid prepared by Wohl and Schweitzer's method (*Abstr.*, 1907, i, 194) to indene.

Dihydroxyhydrindene,  $C_6H_4 \begin{smallmatrix} \diagup CH(OH) \\ \diagdown CH_2 \end{smallmatrix} > CH \cdot OH$ , obtained by heating the chlorohydroxy-derivative with potassium acetate and acetic anhydride and then hydrolysing with potassium hydroxide solution (D 1-3), crystallises from water in brilliant needles, m. p. 158°. The products described by Spilker, m. p. 120°, and by Heusler and Schieffer, m. p. 98—99° (*Abstr.*, 1899, i, 365), are evidently impure. The glycol yields  $\beta$ -hydrindone when warmed with dilute sulphuric acid.

1-Chlorohydrindene,  $C_6H_4 \begin{smallmatrix} \diagup CHCl \\ \diagdown CH_2 \end{smallmatrix} > CH_2$ , is readily formed by passing hydrogen chloride into well cooled indene, and forms a colourless oil which reacts with the greatest readiness with water, yielding indene, 1-hydroxyhydrindene (compare König, *Abstr.*, 1893, i, 587), and 1-hydrindyl ether. 1-Hydroxyhydrindene is odourless and crystallises with great readiness. The methyl ether,  $C_9H_8 \cdot OMe$ , prepared by the action of sodium methoxide on the chloro-derivative, is a colourless oil with b. p. 98°/10 mm., and has an intense odour of acetal.

The *ethyl ether*,  $C_{11}H_{14}O$ , has b. p.  $106-109^{\circ}/16$  mm., and *1-acetoxy-hydrindene*,  $C_{11}H_{12}O_2$ , has b. p.  $135^{\circ}/15$  mm. or  $241^{\circ}$  under atmospheric pressure.

*1-Hydrindyl ether*,  $(C_9H_9)_2O$ , crystallises from alcohol and has m. p.  $51-53^{\circ}$ .

J. J. S.

**Ketens. XXIII. The Reactivity of Halogen Atoms Towards Metals.** HERMANN STAUDINGER, KARL CLAR, and E. CZAKO (*Ber.*, 1911, 44, 1640-1647).—The authors have investigated the behaviour of several halogen derivatives of methane, and of benzyl chloride, benzylidene dichloride,  $\omega$ -chlorodiphenylmethane, benzotrichloride, di- $\omega$ -chlorodiphenylmethane, and  $\omega$ -chlorotriphenylmethane towards zinc in ethereal solution, and find that the removal of halogen takes place readily only in the case of the three compounds last mentioned. From these observations the conclusion is drawn that the substitution of hydrogen by phenyl or chlorine increases the reactivity of the halogen atom. The influence exerted by the chlorine atom is, however, less than that of the phenyl group.

The entrance of substituents into the phenyl groups considerably modifies the reactivity of the chlorine atoms in di- $\omega$ -chlorodiphenylmethane. Whilst di- $\omega$ -chloro-4:4'-dimethoxydiphenylmethane reacts with zinc even more vigorously than di- $\omega$ -chlorodiphenylmethane, di- $\omega$ -chlorodiphenylmethane-4:4'-dicarboxyl chloride and methyl di- $\omega$ -chlorodiphenylmethane-4:4'-dicarboxylate are without action towards this metal.

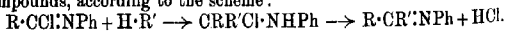
Attention is also called to the fact that acyl chlorides do not react with zinc in ethereal solution, and, therefore, contrary to the usual view, the chlorine atom must be firmly combined with the carbonyl group. A similar behaviour is exhibited by many other halogen compounds, in which the halogen is attached to an unsaturated carbon atom. The apparent mobility of the chlorine atom of acyl chlorides is due, not to its feeble attachment, but to the presence of the unsaturated carbonyl group, which readily combines with water, alcohol, and amines.

The interaction of acyl chlorides with these compounds is represented by the following scheme:



It is also found that acyl chlorides do not react with magnesium to give Grignard compounds, and this is explained by the chlorine atom being firmly combined with the carbonyl group.

The method previously described (Staudinger, *Abstr.*, 1908, i, 654) for the preparation of aldehydes by the action of magnesium on imino-chlorides has been extended to *isobutyrophenylimino-chloride*, *diphenylacetophenylimino-chloride*, and *triphenylacetophenylimino-chloride*, but in no case could a reaction either with magnesium or with zinc be induced. The halogen atom of imino-chlorides is, therefore, firmly attached to the C:N group, and its apparent mobility in many reactions is referred to the intermediate formation of additive compounds, according to the scheme:



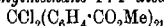
The greater reactivity of imino-chlorides, as compared with acyl chlorides, towards alcohol, water, and amines is due to the greater additive power of the C:N group.

Di-*o*-chlorodiphenylmethane reacts vigorously with zinc in ethereal solution, yielding  $\alpha\beta$ -dichlorotetraphenylethane,  $\text{CPh}_2\text{Cl}\cdot\text{CPh}_2\text{Cl}$ , together with tetraphenylethylene; if the mixture is heated, tetraphenylethylene is the sole product. According to the authors, *o*-chlorodiphenylmethyl is formed as an intermediate product in the reaction, but attempts to convert this into a peroxide by the passage of oxygen into the mixture during the reaction proved unsuccessful. Di-*o*-chlorodiphenylmethane yields with zinc chloride a yellowish-green additive compound.

When treated with zinc in ethereal solution, benzotrichloride gives tolane dichloride ( $\alpha\beta$ -dichloro-*s*-diphenylethylene).

Di-*o*-chloro-4:4'-dimethoxydiphenylmethane, obtained by the action of oxalyl chloride on dimethoxybenzophenone, has m. p. 101–102°, and gives with zinc chloride and mercuric chloride in ethereal solution red additive compounds, which are decomposed by water, yielding the original ketone. It reacts with zinc or mercury in ethereal solution, yielding 4:4':4'':4'''-tetramethoxytetraphenylethylene.

Methyl di-*o*-chlorodiphenylmethane-4:4'-dicarboxylate,



prepared by the interaction of phosphorus pentachloride and methyl benzophenone-4:4'-dicarboxylate, crystallises in colourless needles, m. p. 73°.

iso-Butylphenylimino-chloride,  $\text{CHMe}_2\cdot\text{CCl:NPh}$ , prepared from phosphorus pentachloride and isobutyranilide, is a colourless liquid, b. p. 102–104°/11 mm.

Diphenylacetylphenylimino-chloride,  $\text{CHPh}_2\cdot\text{CCl:NPh}$ , forms colourless crystals, m. p. 90°.

Triphenylacetylphenylimino-chloride,  $\text{CPh}_3\cdot\text{CCl:NPh}$ , has m. p. 132°.

F. B.

**Hydrogenation by means of Calcium and Alcohol.** PIERRE BRETEAU (*Bull. Soc. Chim.*, 1911, [iv], 9, 585–586, and *J. Pharm. Chim.*, 1911, [vii], 3, 580–582).—The process depends on the utilisation of a reaction recorded by Doby (*Abstr.*, 1903, i, 546), in which calcium reacts with ammonia to form hydrogen and calcium amide, the latter being then decomposed by alcohol, giving calcium ethoxide. The application of the method to phenanthrene, which is not reduced by calcium and alcohol alone, is as follows: Fifteen grams of calcium filings are placed in a litre flask provided with a reflux condenser. To this are added 5 grams of phenanthrene in 200 c.c. of alcohol, and the mixture is heated to boiling. Dry ammonia gas is then led into the mixture, and the flame extinguished as soon as hydrogen begins to be evolved. After the calcium is dissolved, the solution is boiled during one hour and then acidified with dilute hydrochloric acid. On cooling, tetrahydrophenanthrene separates as an oil, and may be separated and purified by distillation.

T. A. H.



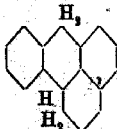
**Phenanthrene Series. XXXV. Nitro- and Amino-phenanthrenes.** JULIUS SCHMIDT and ROGER HIRSH (Ber., 1911, 44, 1488—1503).—1-Nitrophenanthrene has not yet been prepared. The four other possible isomerides are produced by the addition of a mixture of acetic anhydride and nitric acid, D 1.45, to a solution of phenanthrene in hot glacial acetic acid. The separation of the four compounds necessitates a tedious fractional crystallisation from alcohol, whereby 60% of pure 9-nitrophenanthrene, 2% of pure 3-nitrophenanthrene, and 20% each of approximately pure 2-nitrophenanthrene, m. p. 99°, and 4-nitrophenanthrene, m. p. 80—82°, are obtained, the yields being calculated on the crude nitrophenanthrenes; a very small amount of 2-nitrofluorene, produced from a trace of fluorene in the phenanthrene, has also been isolated. 2-Nitrophenanthrene crystallises in pale yellow rosettes, and yields 2-nitrophenanthraquinone when oxidised by chromic and acetic acids. 4-Nitrophenanthrene crystallises in yellow needles, and is oxidised to 4-nitrophenanthraquinone.

A methyl-alcoholic solution of 9-nitrophenanthrene is reduced by zinc dust and methyl-alcoholic ammonia, yielding two modifications of 9-aminophenanthrene, which are separated by crystallisation from alcohol. The less soluble  $\alpha$ -form, m. p. 137—138°, which is the principal product, has been described by Schmidt and Stöbel (Abstr., 1903, i, 691). The  $\beta$ -modification, m. p. 104°, forms a benzoyl derivative, m. p. 199°, identical with that obtained from the  $\alpha$ -modification, yields 9-phenanthrylphenylcarbamide with phenylcarbimide much more slowly than does the  $\alpha$ -modification, and is converted into the  $\alpha$ -modification by acetylation and subsequent hydrolysis. The suggestion is made that the isomerism of the two modifications is due to the different distributions of the double linkings in the phenanthrene nucleus. In large quantities, 9-nitrophenanthrene is reduced most conveniently by tin and hydrochloric acid. 9-Aminophenanthrene forms a *picrolonate*,  $C_{14}H_{11}N_2O_3$ , m. p. 230—231° (decomp.), and a *perchlorate*, m. p. 185°.

4-Aminophenanthrene, m. p. 105°, obtained by reducing 4-nitrophenanthrene with stannous chloride and acetic acid, does not exist in two modifications, and forms a *hydrochloride*, *picrate*, m. p. 216° (decomp.), *picrolonate*, m. p. 195°, decomp. 232°, *benzoyl derivative*, m. p. 224°, and *acetyl derivative*, m. p. 190°; with ethereal phenylcarbimide, it yields *s*-phenyl-4-phenanthrylcarbamide,  $C_{14}H_9 \cdot NH \cdot CO \cdot NHPh$ , m. p. 219—220°, resolidifying and subsequently melting at 279—280°.

C. S.

**Identity of Graebe's *isochrysofluorene* with Dihydrobenzanthrene.** ROLAND SCHOLL and CHRISTIAN SEER (Ber., 1911, 44, 1671—1674).—Graebe's "*isochrysofluorene*" (Abstr., 1894, i, 336), obtained by pyrogenic synthesis from 1-benzyl-naphthalene, has the formula  $C_{17}H_{14}$ , and not  $C_{17}H_{12}$ . After purification by means of the picrate, it has m. p. 79—80°, and is identical with dihydrobenzanthrene (annexed formula: see this vol., i, 676). The red oxidation



product described by Graebe is probably a mixture of benzanthrone and anthraquinone-1-carboxylic acid. F. B.

**New Method of Preparation of Benzylamine and Hexahydrobenzylamine.** PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1911, 163, 160—162).—The authors' method of preparing amines from aliphatic alcohols (*Abstr.*, 1909, i, 292) has been applied by heating the vapour of benzyl alcohol and ammonia in the presence of thorium dioxide; at 330°, benzylamine is the chief product; at 370—380°, dibenzylamine. In practice, a resinous hydrocarbon is gradually deposited on the oxide, and the reaction must be interrupted from time to time in order to revive the catalyst by heating it at a dark red heat in the air.

When the vapour of the benzylamine produced by this method is passed, together with hydrogen, over nickel at 170—180°, considerable quantities of ammonia and toluene are formed, but also a fairly good yield of hexahydrobenzylamine is obtained, identical with that obtained by Démanoff. The experiment fails with benzylamine produced by other methods, probably owing to traces of impurities which destroy the activity of the catalyst. C. S.

**Preparation of Sulphonated Naphthalene Derivatives.** KALLÉ & Co. (D.R.-P. 233934).—When naphthalenepolysulphonic acids are boiled with zinc dust in aqueous solution (preferably in the presence of alkali or ammonium chloride), the sulphonic groups which would be attacked in the case of an alkali fusion are eliminated and replaced by hydrogen. By this means  $\alpha$ -naphthylamine-3:6:8-trisulphonic acid yielded the 3:6-disulphonic acid;  $\alpha$ -naphthylamine-4:6:8-trisulphonic acid, the 4:6-disulphonic acid;  $\alpha$ -naphthylamine-3:5:7-trisulphonic acid, the 3:7-disulphonic acid;  $\alpha$ -naphthylamine-2:5:7-trisulphonic acid, the 2:7-disulphonic acid;  $\beta$ -naphthylamine-3:6:8-trisulphonic acid was converted into the 3:6-disulphonic acid;  $\alpha$ -naphthol-3:5:7-trisulphonic acid into 3:7-disulphonic acid;  $\alpha$ -naphthylamine-3:8-disulphonic acid into 3-monosulphonic acid;  $\alpha$ -naphthylamine-4:8-disulphonic acid yielded naphthionic acid;  $\beta$ -naphthylamine-4:8-disulphonic acid a mixture of the 4- and the 8-monosulphonic acids; and  $\alpha$ -naphthol-8-amino-4:6-disulphonic acid, the  $\alpha$ -naphthol-8-amino-6-sulphonic acid. F. M. G. M.

**Preparation of Sulphonated Aromatic Ammonium Compounds.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 233328).—The sulphonation of aromatic quaternary ammonium bases yields crystalline compounds soluble in water, which probably have the constitution of inner anhydrides.

*Phenylmethylmethylidimethylammonium chloride*, m. p. 124°, prepared from dimethylaniline and  $\alpha$ -chloro- $\beta$ -methylnaphthalene, yields a crystalline *sulphonic acid*.

*Phenylbenzylmethylammonium hydroxide sulphonic anhydride*, large, colourless crystals, is obtained by treating a cooled solution of

*phenylbenzyltrimethylammonium chloride* in concentrated sulphuric acid with fuming acid (23%  $\text{SO}_3$ ), and heating the mixture at  $25-30^\circ$ , when acid containing 70%  $\text{SO}_3$  is employed, a somewhat soluble *disulphonic acid* is produced.

When the *phenylbenzyltrimethylammonium hydroxide sulphonic anhydride* prepared from benzyl chloride and dimethylaniline-*m*-sulphonic acid is sulphonated, an isomeric *disulphonic acid* is obtained.  
F. M. G. M.

The Influence of the Medium and of Light on the Rate of Decomposition of Quaternary Ammonium Salts. EDGAR WEDERKIND, F. PASCHKE, and, in part, W. MAYER (*Ber.*, 1911, 44, 1406-1415. Compare Abstr., 1908, i, 723).—The racemisation of *d*-phenylbenzylmethylpropylammonium bromide in chloroform and in chloroform mixed with other solvents has been studied.

The addition of 20% of a hydroxylic compound, such as methyl or ethyl alcohol, retards racemisation, as does acetone, whereas benzene and carbon disulphide favour decomposition. Solutions of phenylbenzylmethylpropylammonium bromide in mixtures of ethyl alcohol and chloroform, or of ethyl alcohol and ethylene dibromide, have smaller electrical conductivities than solutions of the same concentration in ethyl alcohol alone.

The fact that the racemisation is less in hydroxylic solvents is probably due to the fact that in such solvents the salts are largely ionised, and that for racemisation (thermal dissociation) complete molecules are necessary. Labile salts, such as *l*-phenylbenzylmethyl (methylanilinoethyl) ammonium iodide (Wedekind and Mayer, Abstr., 1909, i, 186), can undergo decomposition in ionising media, but the reaction here is less rapid than in such solvents as chloroform. The reaction has been studied by both polarimetric and electrical conductivity determinations, and the results indicate that autoracemisation is to be attributed to a decomposition into tertiary amine and alkyl halide:  $\text{C}_6\text{H}_5\cdot\text{NMePh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMePh}^+\text{I}^- \rightleftharpoons \text{C}_6\text{H}_5\cdot\text{NMePhI}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMePh} \rightleftharpoons \text{C}_6\text{H}_5\text{I} + \text{NMePh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMePh}$ .

In determining the molecular conductivity it was noticed that the value for this fell to a minimum after about 103 hours, and then increased again, until after 1650 hours the original value was again reached. This is probably due to the fact that the benzyl iodide formed reacts with the solvent alcohol, forming hydrogen iodide and benzyl ethyl ether (compare Halban, Abstr., 1909, i, 627). The solid quaternary ammonium iodide also decomposes when kept, it loses in weight, owing to evolution of benzyl iodide, and its optical activity diminishes from  $-95.98^\circ$  to  $-91.07^\circ$  after 230 days.

The accelerating influence of light on the racemisation of quaternary ammonium salts appears to be of a purely thermal and non-actinic nature (compare Abstr., 1906, i, 419).

When a solution of *d*-phenylbenzylmethylallylammonium hydroxide in chloroform and a little alcohol is kept for forty-eight hours, a slight diminution in the rotation is observable (compare Abstr., 1905, i, 520). This is attributed, not to the decomposition of the base itself, but of a

small amount of quaternary chloride formed by the reaction of the base with the chloroform. J. J. S.

**Preparation of Hydroxyphenylethyldialkylamines.** FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 233069. Compare Abstr., 1906, i, 204, 761, 979; 1907, i, 151, 234, 336).—When the quaternary ammonium salts of *p*-hydroxyphenylethylamines are distilled, they furnish hydroxyphenylethyldialkylamines, and thus confirm the work of Gaebel and Léger, who formulated hordenine as  $\beta$ -*p*-hydroxyphenylethyldimethylamine (Abstr., 1907, i, 151); in the present instance hordenine methiodide, m. p. 230° (prepared from *p*-hydroxyphenylethylamine), furnished on distillation hordenine identical with the product described by these authors.

*Hordenine methochloride* has m. p. 285° (decomp.).

*m*-Ethoxyphenylethylamine hydrochloride, m. p. 160—165° (prepared from *m*-ethoxyphenylpropionamide and sodium hypochlorite), when heated at 100° with alcoholic sodium hydroxide and methyl chloride yields *m*-ethoxyphenylethyltrimethylammonium chloride, m. p. 130°; the methiodide forms colourless needles, m. p. 185—190°, and on distillation in a vacuum furnishes a quantitative yield of *m*-ethoxyphenylethyldimethylamine, a colourless liquid, b. p. 130—133°/15 mm., and convertible by the action of hydrogen iodide into *m*-hydroxyphenylethyldimethylamine, m. p. 103°. F. M. G. M.

**Preparation of Hydroxyphenylethylamines and their Alkyl Ethers.** FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 233551).—It is found that Hofmann's reaction for the conversion of amides into amines can be applied for the preparation of hydroxyphenylethylamines from hydroxyphenylpropionic acids.

$\beta$ -*p*-Methoxyphenylpropionic acid,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , was converted by known methods into *p*-methoxyphenylpropionamide,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ , needles, m. p. 120°, which by treatment with sodium hypochlorite yielded *p*-methoxyphenylethylamine (its hydrochloride has m. p. 210°), and was subsequently converted with hydrogen iodide into *p*-hydroxyphenylethylamine.

Ethyl  $\beta$ -*p*-hydroxyphenylpropionate, m. p. 45°, b. p. 185°/13 mm., furnished an amide, m. p. 125°, and subsequently  $\beta$ -*p*-hydroxyphenylethylamine.

*m*-Ethoxyphenylethylamine hydrochloride has m. p. 160—165°, and *m*-hydroxyphenylethylamine hydrochloride, m. p. 145°.

*o*-Ethoxyphenylethylamine and *o*-hydroxyphenylethylamine hydrochloride have m. p. 210° and m. p. 155° respectively. F. M. G. M.

**The Separation of 6-Chloro-*m*-cresol by the Chlorination of Pure *m*-Cresol, or of the Technical Mixture of *m*- and *p*-Cresols.** ARTHUR LIEBRECHT (D.R.-P. 233118. Compare this vol., i, 537).—Pure 6-chloro-*m*-cresol can be isolated from the technical mixture of *m*- and *p*-cresol by chlorination and subsequent sulphonation of the mixed products with sulphuric acid at 100°. Any 3-chloro-*p*-cresol obtained in the first operation escapes sulphonation, whilst the sulphonated 6-chloro-*m*-cresol is separated in the form of

its sparingly soluble sodium salt, and the sulphonic group eliminated by known methods.

F. M. G. M.

**Preparation of 6-Amino- $\alpha$ -naphthol-5-sulphonic Acid.** KALLE & Co. (D.R.-P. 233105).— $\beta$ -Naphthylamine-1:5-disulphonic acid (prepared by further sulphonation of  $\beta$ -naphthylamine-1-sulphonic acid) when fused at 210–230° with potassium hydroxide yields 6-amino- $\alpha$ -naphthol-5-sulphonic acid, which crystallises from water in slender needles or compact crystals and combines very readily (in alkaline solution) with diazonium salts; its solution in sodium carbonate exhibits a green fluorescence.

F. M. G. M.

**Preparation of Sulphaminobenzoylaminonaphthols and their Sulphonic Acids.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 233117).—Sulphaminobenzoylaminonaphthols, prepared by the action of sulphurous acid on the salts of the corresponding nitrobenzoylaminonaphthols, are readily converted by dilute mineral acid into the corresponding aminobenzoylaminonaphthols; this reaction is capable of extended application, and can be successfully employed in the case of substituted halogen derivatives.

Details for the preparation of sulphaminobenzoyl-5-amino- $\beta$ -naphthol (from *m*-nitrobenzoyl-1:6-aminonaphthol) and of *p*-sulphaminobenzoyl-6-amino- $\alpha$ -naphthol-7-sulphonic acid are given in the patent.

F. M. G. M.

**Preparation of Phenyl Esters of Iodoparaffin Acids.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 233327).—*Phenyl iodoacetate*, glistening needles, m. p. 75–77°, is prepared by boiling together iodoacetic acid, phenol, and carbonyl chloride in benzene-pyridine solution.

*Thymol iodoacetate*, b. p. 176–178°/10 mm., is an oil at the ordinary temperature.

*Guaiacol  $\alpha$ -bromoisovalerate*, colourless, odourless, tasteless crystals, has m. p. 69–70°, and when boiled with potassium iodide yields *guaiacol  $\alpha$ -iodoisovalerate*, m. p. 76–79°.

*Tolyl  $\alpha$ -iodoisovalerate* is a viscous, oily fluid which slowly solidifies.

*Guaiacol  $\alpha$ -iodo- $\beta$ -methylheptanoate*,  $C_8H_7 \cdot CHMe \cdot CHI \cdot CO_2 \cdot C_6H_4 \cdot OMe$ , and its bromo-analogue form oily, yellow, tasteless, odourless, fluids. *Guaiacol  $\alpha$ -iodo-*n*-butyrate* has b. p. 185°/10 mm., and *guaiacol  $\alpha$ -bromo-*n*-butyrate*, b. p. 165°/10 mm.

*Guaiacol iodobenenate*, a thick, honey-like oil, is prepared from iodobenenic acid and guaiacol in the presence of phosphorus trichloride.

*Quinol di- $\alpha$ -bromoisovalerate*,  $(C_6H_5Br \cdot CO_2)_2C_6H_4$ , odourless, tasteless needles, has m. p. 53°; *quinol di- $\alpha$ -iodoisovalerate* has similar properties and m. p. 85–87°.

*Guaiacol iodostearate* is a yellowish-red oil, and *guaiacol  $\alpha$ -iodoisobutyrate* has b. p. 160–175°/15 mm. These compounds are of therapeutic value.

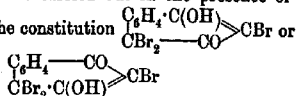
F. M. G. M.

**Naphtharesorcinol** [1:3-Dihydroxynaphthalene] and **4-Amino-β-naphthol**. RICHARD MEYER and KURT WOLFSLEBEN (*Ber.*, 1911, 44, 1958—1966).—An account of the preparation and properties of some derivatives of 1:3-dihydroxynaphthalene and of 4-amino-β-naphthol, obtained in an unsuccessful attempt to prepare a meta-quinone of the naphthalene series.

When 1:3-dihydroxynaphthalene (1 mol.) is treated with bromine (4 atoms) in glacial acetic acid solution at a low temperature, 2:4-dibromo-1:3-dihydroxynaphthalene,  $C_{10}H_6Br_2(OH)_2$ , crystallising in needles, m. p. 128—129°, is produced; the acetyl derivative,  $C_{10}H_6Br_2(OAc)_2$ , has m. p. 125°.

**Tribromo-1:3-dihydroxynaphthalene**,  $C_{10}H_4Br_3(OH)_2$ , prepared by the action of bromine (8 atoms) on 1:3-dihydroxynaphthalene in a similar manner, crystallises in silvery needles, m. p. 186°; the acetyl derivative,  $C_{10}H_4Br_3(OAc)_2$ , crystallises in needles or prisms of monoclinic habit, m. p. 182°; the benzoyl derivative, felted needles, has m. p. 129° (not sharp).

When the bromination is carried out in the presence of water at 2°, an isomeride having the constitution



is obtained. This forms yellow crystals, m. p. 85° (decomp.), and when heated with acetyl chloride loses bromine and yields the above-mentioned acetyl derivative of 2:4-dibromo-1:3-dihydroxynaphthalene.

Zincke and Egly's 2:4-tetrachloro-1:3-diketotetrahydronaphthalene (*Abstr.*, 1898, i, 439) is obtained by the action of chlorine on 1:3-dihydroxynaphthalene in glacial acetic acid solution.

When air is passed through an alkaline solution of 1:3-dihydroxynaphthalene, β-hydroxy-α-naphthaquinone is produced.

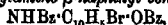
Attempts to oxidise substituted derivatives of 1:3-dihydroxynaphthalene yielded tarry products.

**4-Benzoylamino-β-naphthyl benzoate**,  $NHBz \cdot C_{10}H_6 \cdot OBz$ , forms colourless needles, m. p. 188°.

**Ethyl 3-hydroxy-α-naphthylloxamate**,  $OH \cdot C_{10}H_7 \cdot NH \cdot CO \cdot CO_2Et$ , prepared by the interaction of 4-amino-β-naphthol and ethyl oxalate, crystallises in pale yellow, felted needles, m. p. 171°. When hydrolysed with aqueous sodium hydroxide, this yields 3-hydroxy-α-naphthylloxamic acid, which crystallises in stellar aggregates of needles, m. p. 219° (decomp.); the amide,  $OH \cdot C_{10}H_7 \cdot NH \cdot CO \cdot CO \cdot NH_2$ , forms yellow, flat needles, m. p. 260°.

**N-3-Hydroxy-α-naphthylphthalamic acid**,  $OH \cdot C_{10}H_7 \cdot NH \cdot CO \cdot C_6H_4 \cdot CO_2H$ , obtained by heating 4-amino-β-naphthol with phthalic anhydride in xylene solution, has m. p. 220° (decomp.).

**N-β-Naphthylphthalamic acid**,  $C_{10}H_7 \cdot NH \cdot CO \cdot C_6H_4 \cdot CO_2H$ , and **N-β-naphthylphthalamic acid** may be prepared from the corresponding naphthylamines in a similar manner (compare Piutti, *Abstr.*, 1886, 172, 473).

1(or 3)-Bromo-4-benzoylamino- $\beta$ -naphthyl benzoate,

obtained by brominating the benzoyl derivative of 4-amino- $\beta$ -naphthol in alcoholic solution, forms colourless crystals.

1:3-Dibromo-4-acetylamino- $\beta$ -naphthol,  $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{Br}_2 \cdot \text{OH}$ , is prepared by the interaction of bromine and 4-acetylamino- $\beta$ -naphthol in glacial acetic acid solution; it crystallises in stout needles, m. p.  $210^\circ$  (decomp.), and on treatment with acetic anhydride and a little sulphuric acid yields 1:3-dibromo-4-acetylamino- $\beta$ -naphthyl acetate,  $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{Br}_2 \cdot \text{OAc}$ , m. p.  $230^\circ$ , which is also obtained by brominating and subsequently acetylating 4-amino- $\beta$ -naphthol. F. B.

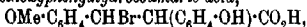
Action of Phenol on Methylcoumaric Acid Dibromide and the Constitution of Werner's "Hydroxyphenylcoumaran." RICHARD STÖRMER and C. FRIEDEL (*Ber.*, 1911, 44, 1838—1853. Compare Werner, *Abstr.*, 1906, i, 180).—The supposed 2-hydroxy-

phenylcoumaran,  $\text{C}_6\text{H}_4 \cdot \begin{array}{c} \text{O} \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH} \end{array}$ , prepared by Werner (*loc. cit.*)

by the action of phenol on methylcoumaric acid dibromide, is shown to be 4'-hydroxy-2-methoxystilbene,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ . On oxidation, o-methoxybenzoic acid and anisic acid are formed. The chief product of the interaction of the dibromide and phenol is  $\beta$ -bromo- $\alpha$ -methoxyphenylhydrocoumaric acid. This amounts to 65%; some is decomposed into hydroxystilbene during the reaction, and it is readily converted into this by treatment with sodium carbonate.

The constitution of 4'-hydroxy-2-methoxystilbene is established by its synthesis from *p*-hydroxyphenylacetic acid and o-methoxybenzaldehyde; these condense to hydroxymethoxystilbenecarboxylic acid, which is heated with soda lime.

4'-Hydroxy-2-methoxystilbene,  $\text{C}_{15}\text{H}_{14}\text{O}_2$ , regarded by Werner as hydroxyphenylcoumaran,  $\text{C}_{14}\text{H}_{12}\text{O}_2$ , is prepared by mixing equal parts of methylcoumaric acid dibromide and phenol and heating on the water-bath; it has m. p. sharp at  $149^\circ$ .

 $\beta$ -Bromo- $\alpha$ -methoxyphenylhydrocoumaric acid,

crystallises in colourless, rhombic plates, m. p.  $185$ — $186^\circ$ .

2:4'-Dimethoxystilbene, obtained by the action of methyl sulphate on the monomethyl ether, forms blue fluorescing platelets, m. p.  $93^\circ$  (compare Werner, *loc. cit.*).

2-Methoxy-4'-ethoxystilbene crystallises in blue, fluorescing, broad needles, m. p.  $70^\circ$ .

4'-Benzoyloxy-2-methoxystilbene separates in colourless needles of silky lustre, m. p.  $123^\circ$ . The corresponding *p*-nitrobenzoyl derivative forms lustrous, golden-yellow plates, m. p.  $148^\circ$ .

The dibromide of the above dimethoxy-derivative is a colourless powder, m. p.  $133^\circ$ ; the dibromide of the acetyl derivative crystallises in small, colourless plates, m. p.  $170^\circ$ .

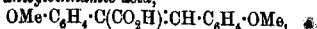
On reduction of dimethoxystilbene in alcohol with sodium, 2:4'-dimethoxydibenzyl is obtained as a clear, transparent oil, which becomes solid in ice, m. p.  $45^\circ$ .

The reduction of methoxyhydroxystilbene is more difficult, and is

carried out in amyl alcohol. *4'-Hydroxy-2-methoxydibenzyl* forms colourless, long needles, m. p. 63°. Methyl sulphate converts it into the dimethyl ether, m. p. 45°. The *p*-nitrobenzoyl ether crystallises in creamy-yellow plates, m. p. 135°.

Oxidation of both methoxyhydroxystilbene and its dihydro-derivative with permanganate gave *o*-methoxybenzoic acid; the oxidation of the dimethoxystilbene gave a mixture of *o*- and *p*-methoxybenzoic acids.

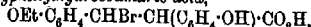
*p*-Methoxy-*o*-anisylcinnamic acid,



prepared by the Perkin synthesis from anisaldehyde and sodium *o*-methoxyphenylacetate, crystallises in colourless needles, m. p. 191°. On distillation with soda lime, 2:4'-dimethoxystilbene is obtained.

*α*-*p*-Methoxyphenylcoumaric acid,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C}(\text{C}_6\text{H}_4 \cdot \text{OH}) \cdot \text{CO}_2\text{H}$ , from sodium *p*-hydroxyphenylacetate and *o*-methoxybenzaldehyde, crystallises in renniform aggregates of needles, m. p. 202°. On distillation with soda lime, methoxyhydroxystilbene, m. p. 149°, is obtained. Methyl sulphate converts it into the di-ether, and, on hydrolysis, *α*-*p*-methoxymethylcoumaric acid, m. p. 198°, is formed.

On condensation of ethylcoumaric acid dibromide with phenol, *β*-bromo-*α*-ethoxyphenylhydrocoumaric acid,



is obtained, crystallising in needles, m. p. 166°. On treatment with sodium carbonate, *4'-hydroxy-2-ethoxystilbene* is obtained; it crystallises in blue, fluorescing needles, m. p. 107°. The compound 2-methoxy forms short, blue, fluorescing plates, m. p. 60°. E. F. A.

Syntheses by means of Sunlight. HEINRICH KLINGER [with WALTER ROERDANSZ] (*Annalen*, 1911, 382, 211—221. Compare Klinger and Standke, *Abstr.*, 1891, 900; Klinger and Kolvenbach, 1898, i, 467).—Valeroylquinol and benzoylquinol can be prepared by the action of zinc chloride on quinol and valeric or benzoic acid. The yields, however, are not good, as appreciable amounts of dark-coloured products are also formed. The dibenzoyl derivative of quinol,  $\text{C}_6\text{H}_4(\text{O} \cdot \text{COPh})_2$ , is also formed when benzoic acid is used.

Mixtures of phenanthraquinone, benzene, and various aldehydes when exposed to bright sunlight in narrow sealed tubes undergo condensation. Most of the experiments were conducted in tubes 70 cm. long and 2 cm. wide.

Phenanthraquinone (10 grams), salicylaldehyde (6 c.c.), and benzene (50 c.c.) at the end of twenty days yield the *monosalicyloyl* derivative

of phenanthraquinol,  $\text{C}_6\text{H}_4 \langle \text{C}(\text{OH}) \rangle \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , which crys-

tallises from benzene or alcohol in colourless, glistening needles, m. p. 188°. It is hydrolysed by alkalis to the quinol, and this, on shaking in contact with air and the alkaline liquid, gives the quinone. The

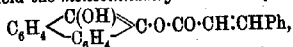
*diacetyl* derivative,  $\text{C}_6\text{H}_4 \langle \text{C}(\text{OAc}) \rangle \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OAc}$ , crystallises from

a mixture of alcohol and benzene in well-developed, strongly refractive octahedra, m. p. 143°, or from hot alcohol in colourless, glistening needles, m. p. 151°. The corresponding *dibenzoyl* derivative,  $\text{C}_{28}\text{H}_{22}\text{O}_6$ , prepared by heating the salicyloylphenanthraquinol with five times



its weight of benzoic anhydride at 150–160° for thirty minutes, crystallises from benzene or glacial acetic acid in colourless, flat needles, m. p. 216–217°. Cold anhydrous nitric acid reacts with the salicyloyl derivative, yielding phenanthraquinone and 3:5-dinitro-salicylic acid.

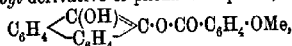
Phenanthraquinone, cinnamaldehyde, and benzene, at the end of fourteen days, yield the *monocinnamoyl* derivative,



which crystallises from benzene or glacial acetic acid in colourless needles, m. p. 193°, or from alcohol in canary-yellow needles, lts

*acetyl* derivative,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C(OH)} \diagdown \\ \diagdown \text{C}_6\text{H}_4 \diagup \end{array} \text{C} \cdot \text{O} \cdot \text{CO} \cdot \text{CH} \cdot \text{CHPh}$ , crystallises in colourless prisms, m. p. 154°, and yields a *dibromide*,  $\text{C}_{26}\text{H}_{18}\text{O}_4\text{Br}_2$ , in the form of colourless, slender needles, m. p. 211°. The corresponding *benzoyl* derivative,  $\text{C}_{30}\text{H}_{20}\text{O}_4$ , forms colourless crystals, m. p. 218°.

The *monoisotoyl* derivative of phenanthraquinol,

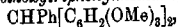


crystallises from benzene in slender, glistening plates, m. p. 232°, and yields an *acetyl* derivative,  $\text{C}_{28}\text{H}_{18}\text{O}_5$ , in the form of colourless, rhombic plates, m. p. 175°, and a *benzoyl* derivative,  $\text{C}_{30}\text{H}_{20}\text{O}_5$ , m. p. 193°.

*Monofurfurylphenanthraquinol*,  $\text{C}_{19}\text{H}_{12}\text{O}_4$ , crystallises from benzene in well-developed, ruby-red prisms, m. p. 193°, or in orange-coloured crystals with the same m. p. The crystals have  $a : c = 1 : 0.3111$ .

J. J. S.

**New Derivatives in the Triphenylmethane Series.** THOM SZÉKI (*Ber.*, 1911, 44, 1476–1481).—In consequence of the labile character of the hydrogen atom in the para-position to a methoxy-group in hydroxyquinol trimethyl ether (Abstr., 1907, i, 45; 1910, i, 837), the ether condenses readily with aromatic aldehydes to form derivatives of triphenylmethane of the type  $\text{CHR}[\text{C}_6\text{H}_4(\text{OMe})_2]_2$ . The condensation is effected in glacial acetic acid by hydrochloric acid, D 1.19, at the ordinary temperature. Thus benzaldehyde, *m*-nitrobenzaldehyde, and *p*-nitrobenzaldehyde respectively yield 2:4:5:2':4':5'-hexamethoxytriphenylmethane,



m. p. 130.5°, 3-nitro-2':4':5':2'':4'':5''-hexamethoxytriphenylmethane, m. p. 117°, citron-yellow needles, and 4-nitro-2':4':5':2'':4'':5''-hexamethoxytriphenylmethane, m. p. 117°, citron-yellow crystals. The following compounds have been obtained from vanillin, salicylaldehyde, *p*-hydroxybenzaldehyde, piperonal, and protocatechu-aldehyde respectively: 4-hydroxy-3:2':4':5':2'':4'':5''-heptamethoxytriphenylmethane, m. p. 187.5°; 2-hydroxy-2':4':5':2'':4'':5''-hexamethoxytriphenylmethane, m. p. 176° (acetate, m. p. 148–149°); 4-hydroxy-2':4':5':2'':4'':5''-hexamethoxytriphenylmethane, m. p. 205°; 3:4-methylenedioxy-2':4':5':2'':4'':5''-hexamethoxytriphenylmethane, m. p. 137°; 3:4-dihydroxy-2':4':5':2'':4'':5''-hexamethoxytriphenylmethane, m. p. 202° (diacetate, m. p. 124°).

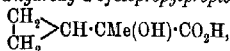
The preceding compounds, excepting those prepared from the nitrobenzaldehydes and salicylaldehyde, react with bromine in benzene to form bromotrimethoxybenzene and brown or bluish-violet substances, which are very probably derivatives of diphenylmethane. C. S.

**Transformations of cycloPropyldimethylcarbinol.** NICOLAI M. KLINER and W. Klawikordoff (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 595—608).—In the synthesis of cyclopropyldimethylcarbinol by the action of magnesium methyl iodide on ethyl cyclopropylcarboxylate (compare Zelinsky, Abstr., 1901, i, 660; 1902, i, 70), an appreciable proportion of an unsaturated iodide,  $C_6H_{11}I$ , b. p. 176—180°/752 mm. (decomp.),  $D_4^{20}$  1.4305, is obtained. When freed from all traces of this iodide, cyclopropyldimethylcarbinol has b. p. 124.5—125°/752 mm.,  $D_4^{20}$  0.8844,  $n_D^{20}$  1.4330 (compare Bruylants, Abstr., 1909, i, 226).

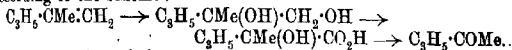
The hydrocarbon obtained by Alexceff (Abstr., 1905, i, 639) by the action of acetic anhydride on cyclopropyldimethylcarbinol, and described by this author as dimethylmethylenetrimethylene, is

found to be  $\beta$ -cyclopropyl- $\Delta^2$ -propylene,  $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} > CH \cdot CMe \cdot CH_2$ , b. p.

71.1—71.5°/772 mm.,  $D_4^{20}$  0.7523,  $n_D^{20}$  1.4252, and is accompanied by acetyl derivatives giving on hydrolysis a mixture of alcohols, b. p. 124—160°, the nature of which was not investigated. Oxidation of this hydrocarbon by means of permanganate yields: (1) acetyltrimethylene; (2)  $\alpha$ -hydroxy- $\alpha$ -cyclopropylpropionic acid,



which forms colourless, acicular needles, m. p. 75.5°, gives a hydrate,  $2C_6H_9O_3 \cdot H_2O$ , m. p. 54—55°. This oxidation probably takes place according to the scheme:



By the action of fuming hydrobromic acid, hydroxycyclopropylpropionic acid yields (1) in the cold,  $\alpha$ -methylene- $\delta$ -bromovaleric acid,  $CH_2Br \cdot CH_2 \cdot CH_2 \cdot C(CH_2Br) \cdot CO_2H$ , colourless, rhombic plates, m. p. 68°; (2) in a sealed tube at 100°,  $\delta$ -bromo- $\alpha$ -bromomethylvaleric acid,  $CH_2Br \cdot CH_2 \cdot CH_2 \cdot CH(CH_2Br) \cdot CO_2H$ , plates, m. p. 88—90°.

When heated with dilute sulphuric acid in a sealed tube,  $\beta$ -cyclopropyl- $\Delta^2$ -propylene yields the hexylene oxide obtained by Zelinsky (Abstr., 1902, i, 70). Treatment of this oxide or of cyclopropyldimethylcarbinol by fuming hydrobromic acid yields  $\beta$ - $\delta$ -dibromo- $\beta$ -methylpentane,  $CH_3Br \cdot CH_2 \cdot CH_2 \cdot CMe_2Br$ , b. p. 104—104.5°/23 mm.,  $D_4^{20}$  1.5865—1.5902,  $n_D^{20}$  1.5045—1.5051. The action of alcoholic potassium hydroxide on this dibromo-derivative yields:

(1)  $\delta$ -Methyl- $\Delta^2$ -pentadiene,  $CH_3 \cdot CH \cdot CH \cdot CMe_2$ , b. p. 76—77.5°/766 mm.,  $D_4^{20}$  0.7193,  $n_D^{20}$  1.4491. The structure of this hydrocarbon is decided by the considerable excess of the experimental (30.59) value of the molecular refraction over the calculated value (28.93) (compare Brühl, Trans., 1907, 115; Reif, Abstr., 1908, i, 847).  $\delta$ -Methyl- $\Delta^2$ -pentadiene is found to be identical with the compound described by Bruylants (*loc. cit.*) as  $\beta$ -cyclopropylpropylene.

(2) *ε*-Ethoxy- $\beta$ -methyl- $\Delta^8$ -amylene,  $\text{OEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CMe}_3$ , b. p. 142.5—143.5°/766 mm.,  $D_4^{20}$  0.7975,  $n_D^{20}$  1.4182. On oxidation with permanganate, it yields acetone and other products.

The action of hydriodic acid on cyclopropyldimethylcarbinol and reduction of the iodo-derivative thus obtained by means of sodium yields  $\beta$ -methylpentane.

T. H. P.

Dehydration of Alkyl- and Benzyphenyl-*tert*-butylcarbinols. (Mile.) PAULINE LUCAS (*Compt. rend.*, 1911, 152, 1771—1774. Compare Abstr., 1910, i, 378).—A further examination of the hydrocarbons obtained previously by dehydrating the product of the action of an organo-magnesium halide on a trialkylacetophenone. The substance to which the formula  $\text{CMe}_3\cdot\text{CPh}\cdot\text{CH}_2$  was ascribed appears to be a mixture of a liquid having this constitution with 1-phenyl-2:2-dimethylcyclopropane, since on oxidation with chromic acid it furnishes acetone, acetophenone, and trimethylacetophenone; the latter ketone was characterised by its semicarbazone, m. p. 195°.

Magnesium ethyl iodide acts on trimethylacetophenone to give  $\gamma$ -phenyl- $\beta\beta$ -dimethylpentan- $\gamma$ -ol,  $\text{CMe}_3\cdot\text{CEtPh}\cdot\text{OH}$ , b. p. 115—116°/15 mm. When this is boiled with formic acid, it yields a single hydrocarbon,  $\gamma$ -phenyl- $\delta\delta$ -dimethyl- $\Delta^8$ -hexene,  $\text{CMe}_3\cdot\text{CPh}\cdot\text{CHMe}$ , b. p. 90—95°/12 mm., the constitution of which follows from the formation of carbon dioxide and trimethylacetophenone on oxidation.

The hydrocarbon from  $\gamma\delta$ -diphenyl- $\beta\beta$ -dimethylbutan- $\gamma$ -ol similarly gives carbon dioxide, benzoic acid, trimethylacetophenone, and a substance,  $\text{C}_{18}\text{H}_{20}\text{O}$ , b. p. 195—200°/15 mm. It is, therefore, probably  $\alpha\beta$ -diphenyl- $\gamma\gamma$ -dimethyl- $\Delta^8$ -butylene,  $\text{CMe}_3\cdot\text{CPh}\cdot\text{CHPh}$ . The unidentified product of oxidation appears not to contain a carbonyl group.

W. O. W.

Preparation of Hydroxybenzyl Alcohol, Hydroxybenzaldehyde, and Hydroxybenzoic Acids. FAIRZ RASCHIG (D.R.P. 233631).—When substituted phenols containing an acid radicle in place of the hydroxyl hydrogen are quantitatively chlorinated at a temperature of 150—180°, derivatives containing chlorine in the side-chain only are obtained.

$\omega$ -Chloro-*o*-tolyl carbonate,  $\text{CO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Cl})_2$ , m. p. 79°, prepared from *o*-tolyl carbonate, furnishes when boiled with calcium carbonate and water under 4—5 atmospheres pressure a satisfactory yield of *o*-hydroxybenzyl alcohol (saligenin).

$\omega$ -Dichloro-*o*-tolyl carbonate,  $\text{CO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CHCl}_2)_2$ , m. p. 73°, b. p. 247°/30 mm., when similarly treated furnishes salicylaldehyde.

$\omega$ -Dichloro-*p*-tolyl carbonate, m. p. 108°, is decomposed into *p*-hydroxybenzaldehyde, whilst  $\omega$ -trichloro-*m*-tolyl carbonate,  $\text{CO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CCl}_3)_2$ , an unstable oil, yields *m*-hydroxybenzoic acid.

*o*-Tolyl phosphate,  $\text{PO}(\text{O}\cdot\text{C}_6\text{H}_4\text{Me})_3$ , an oil, b. p. 410°/760 mm., prepared from *o*-cresol and phosphoryl chloride, yields  $\omega$ -dichloro-*o*-tolyl phosphate, m. p. 78°, and subsequently salicylaldehyde.

*o*-Tolyl phosphite,  $\text{P}(\text{O}\cdot\text{C}_6\text{H}_4\text{Me})_3$ , prepared from *o*-cresol and phosphorus trichloride on chlorination, yields first an additive product,  $(\text{CH}_3\cdot\text{C}_6\text{H}_4\text{O})_3\text{PCl}_2$ , and subsequently a viscous oil consisting chiefly of

*o*-dichloro-*p*-tolyl dichlorophosphate,  $(\text{CHCl}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{O})_2\text{PCl}_2$ , and on hydrolysis, salicylaldehyde.

*o*-Tolyl benzenesulphonate,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{O} \cdot \text{SO}_2\text{Ph}$ , yields *o*-dichloro-*o*-tolyl benzenesulphonate, needles, m. p.  $73^\circ$ , and salicylaldehyde on hydrolysis.

*o*-Dichloro-*m*-tolyl benzoate,  $\text{OBz} \cdot \text{C}_6\text{H}_3(\text{CHCl}_2)_2$ , obtained from *m*-tolyl benzoate, is an unstable oil, which cannot be distilled even in a vacuum, and on hydrolysis yields a mixture of benzoic acid and *m*-hydroxybenzaldehyde.

F. M. G. M.

Catalytic Esterification of Aromatic Acids in the Wet Way. JEAN B. SENDERENS and J. ABOULENC (*Compt. rend.*, 1911, 152, 1855—1857. Compare this vol., i, 600).—Contrary to what has been noticed in the case of the aliphatic acids, the extent and rapidity of the esterification of benzoic acid increases with the amount of sulphuric acid employed as a catalyst, but not with that of potassium hydrogen sulphate or hydrated aluminium sulphate, which only give poor yields of the ester. The same observation applies to salicylic acid and the toluic acids, but phenylacetic and phenylpropionic acids more closely resemble acetic acid in this respect.

W. O. W.

Alkyl Chloro- and Bromo-anthranilates. PAUL FREUNDLER (*Bull. Soc. chim.*, 1911, [iv], 9, 605—608).—Methyl 5-chloroanthranilate (Abstr., 1907, i, 158) is readily obtained by direct chlorination by Flürscheim's method (*Trans.*, 1908, 93, 1772), using a mixture of acetic and hydrochloric acids as a solvent. A small amount of the 3:5-dichloro-ester is formed in the reaction, but this is easily separated owing to its insolubility in dilute hydrochloric acid. Methyl 3:5-dichloroanthranilate, m. p.  $63$ — $64^\circ$ , crystallises in colourless needles, and is very soluble in alcohol.

The process used by Wheeler (Abstr., 1909, i, 382) for the bromination of anthranilic acid gives good results for the methyl ester. Methyl 5-bromoanthranilate, m. p.  $74^\circ$ , crystallises in yellowish-white prisms. The dibromo-ester (? 3:5) formed simultaneously has m. p.  $84^\circ$ , crystallises in slender needles, and is soluble in alcohol.

T. A. H.

Further Investigation of Certain Derivatives of *o*-Sulphobenzoic Acid. PHILIP H. COBB and GEORGE P. FULLER (*Amer. Chem. J.*, 1911, 45, 605—611).—It has been shown by Cobb (Abstr., 1908, i, 499) that the substance, m. p.  $162$ — $163^\circ$ , obtained by Remsen and Saunders (Abstr., 1895, i, 474) and List and Stein (Abstr., 1898, i, 584) by the action of benzene and aluminium chloride on a mixture of the chlorides of *o*-sulphobenzoic acid, is diphenylbenzylsulphone,  $\text{C}_6\text{H}_5\text{C}(\text{SO}_2)_2\text{C}_6\text{H}_5$ , and can be prepared by the action of magnesium phenyl bromide on *o*-sulphobenzoic anhydride.

Sachs (Abstr., 1904, i, 877) has stated that when "methyl-saccharin" is treated with magnesium phenyl bromide, triphenylcarbinol-*o*-sulphonmethylamide is produced, which, when heated with concentrated hydrochloric acid in a sealed tube at  $150^\circ$ , yields a com-

pound, m. p. 210°, which he regarded as diphenylbenzylsulphone. On repeating these experiments, it has been found that Sachs' compound (m. p. 210°) is not diphenylbenzylsulphone, but the lactam,  $C_6H_5 \langle \begin{smallmatrix} CPh_2 \\ SO_2 \end{smallmatrix} \rangle NMe$ , and that the same substance is produced when triphenylcarbinol-*O*-sulphonemethylamide is treated with concentrated sulphuric acid for twelve hours at 50°.

When *di-p-tolylphenylcarbinol-O-sulphonemethylamide*,  $OH \cdot C(C_6H_4Me)_2 \cdot C_6H_4 \cdot SO_2 \cdot NHMe$ , m. p. 243° (uncorr.), obtained by the action of magnesium *p*-tolyl bromide on "methylsaccharin," is heated with concentrated hydrochloric acid for fourteen hours at 150°, or with concentrated sulphuric acid at 70°, no change takes place and the substance can be recovered. E. G.

**Ketens. XX. Attempts to Prepare Quinoketens.** HERMANN STAUDINGER and KARL CLAR (*Ber.*, 1911, 44, 1623—1633).—An account of unsuccessful attempts to synthesise the following quinonoid ketens: (I)  $CO \cdot C_6H_4 \cdot CO$ , (II)  $CPh_2 \cdot C_6H_4 \cdot CO$ , (III)  $CO \cdot C_6H_4 \cdot C \cdot C_6H_4 \cdot CO$ .

*Terephthaloyl bromide*, prepared by the action of phosphorus pentabromide on the corresponding acid in the presence of phosphoryl bromide, crystallises from light petroleum in long, colourless needles, m. p. 85°. When heated with zinc in ethereal solution, it yields ethyl terephthalate; no evidence of the formation of dioxoquinodimethane (I) was obtained.

Diphenyl-*p*-tolylcarbinol is prepared most readily by the interaction of magnesium phenyl bromide and phenyl *p*-tolyl ketone (compare Bistrzycki and Gyr, *Abstr.*, 1904, i, 315; Acree, *ibid.*, 409). It is converted by prolonged boiling with dilute nitric acid into triphenylcarbinol-*p*-carboxylic acid, m. p. 203—205° (compare Bistrzycki and Gyr, *loc. cit.*), which, on treatment with phosphorus pentachloride or thionyl chloride, yields *ω*-chlorotriphenylmethane-4-carboxyl chloride,  $CPh_2Cl \cdot C_6H_4 \cdot COCl$ . The latter forms colourless crystals, m. p. 80—81°, is very stable towards water, and, when treated with aniline in ethereal solution, yields *ω*-anilino triphenylmethane-4-carboxylic acid,  $C_6H_5 \cdot NH \cdot CPh_2 \cdot C_6H_4 \cdot CO_2H$ , m. p. 182°.

Triphenylmethane-4-carboxylic acid, m. p. 165° (compare O. Fischer and Albert, *Abstr.*, 1893, i, 196), obtained by reducing triphenylcarbinol-*p*-carboxylic acid with phosphorus and iodine in glacial acetic acid solution, is converted by thionyl chloride into the corresponding chloride,  $CHPh_2 \cdot C_6H_4 \cdot COCl$ , which forms white crystals, m. p. 89—90°; the *anilide*,  $C_{26}H_{21}ON$ , has m. p. 196°. All attempts to prepare diphenyloxoquinodimethane (II) either by the removal of hydrogen chloride from triphenylmethane-4-carboxyl chloride by means of quinoline and tripropylamine, or by the action of zinc on *ω*-chlorotriphenylmethane-4-carboxyl chloride, proved unsuccessful.

When an ethereal solution of the last-named compound is heated with zinc, or shaken with mercury in an atmosphere of carbon dioxide, an intense reddish-violet coloration, due to the formation of triphenylmethyl-4-carboxyl chloride,  $-CPh_2 \cdot C_6H_4 \cdot COCl$ , is produced. The violet

solution of the triphenylmethyl derivative is at once decolorised on exposure to air, or by the addition of bromine; when treated with aniline it yields *triphenylmethyl-4-carboxylanilide*.

The *peroxide*,  $C_{40}H_{28}O_4Cl_2$ , obtained by passing a stream of air through an ethereal solution of the chloride, crystallises in white plates, m. p.  $168^\circ$  (decomp.), and gives the usual peroxide reactions. It is decomposed by concentrated sulphuric acid, yielding triphenylcarbinol-*p*-carboxylic acid.

*Methyl triphenylcarbinol-4-carboxylate*,  $C_{21}H_{18}O_3$ , prepared by the action of methyl iodide on the corresponding silver salt, has m. p.  $119^\circ$  and, on treatment with phosphorus pentachloride or oxalyl chloride, yields *methyl  $\omega$ -chlorotriphenylmethane-4-carboxylate*, which forms a pale yellow, amorphous mass. When an ethereal solution of the chloro-ester is shaken with mercury, a reddish-violet solution of *methyl triphenylmethyl-4-carboxylate* is obtained.

The solution is stable towards water and aniline, but is decolorised on exposure to air, or by the addition of bromine. The *peroxide* forms a white powder, m. p.  $171.5^\circ$  (decomp.).

Benzophenone-4:4'-dicarboxylic acid is best prepared by heating di-*p*-tolyl ketone with dilute nitric acid and subsequently oxidising the monocarboxylic acid thus obtained with potassium permanganate in alkaline solution.

With phosphorus pentachloride it yields *di- $\omega$ -chlorodiphenylmethane-4:4'-dicarboxyl chloride*,  $CCl_2(C_6H_4COCl)_2$ , which forms colourless crystals, m. p.  $78^\circ$ , and undergoes no change when heated with zinc in ethereal or ethyl acetate solution.

Benzophenone-4:4'-dicarboxylanilide,  $C_{27}H_{20}O_3N$ , has m. p.  $302^\circ$ .

F. B.

**Action of Sunlight on *allo*-Cinnamic Acid.** ANNE W. K. DE JONG (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 100—101. Compare Riiber, *Abstr.*, 1902, i, 785).—*allo*-Cinnamic acid (m. p.  $41$ – $42^\circ$ ) exposed to sunlight for some days became opaque and was no longer completely soluble in ether. The insoluble portion, dissolved in ammonia, gave a heavy precipitate with barium chloride. The acid from the barium salt melted at  $206^\circ$ , the m. p. being unchanged by mixing with  $\beta$ -truxillic acid from the coca-acids. The ether extract yielded, in addition, ordinary cinnamic acid,  $\alpha$ -truxillic acid, and a trace of oil.

J. D. K.

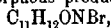
**Ketens. XXI. Attempts to Prepare Alleneketens.** HERMANN STAUDINGER and E. OTT (*Ber.*, 1911, 44, 1633—1637).—Attempts to synthesise allene-ketens of the type  $CR_2C:CO$  by the action of zinc on  $\alpha$ -bromo- $\alpha\beta$ -unsaturated acyl chlorides were unsuccessful.

*$\alpha$ -Bromocinnamoyl bromide*, obtained by the interaction of phosphorus pentabromide and the corresponding acid in benzene solution, has b. p.  $170^\circ/23$  mm. The chloride is best prepared by the action of thionyl chloride on the acid (compare Anschütz and Selden, *Abstr.*, 1887, 829); when heated with zinc in ethyl acetate solution, it yields

a brown, amorphous substance, m. p. 206°, which contains chlorine, but is free from bromine.

In the preparation of  $\beta\beta$ -dimethylacrylic acid from ethyl  $\alpha$ -bromo-isovalerate, the removal of hydrogen bromide is most readily effected by means of quinoline; the chloride has b. p. 145—150°; the anilide, m. p. 126—127°.

$\alpha$ -Bromo- $\beta\beta$ -dimethylacrylic acid is obtained in almost quantitative yield by the action of alcoholic sodium ethoxide on  $\alpha\beta$ -dibromo-isovaleric acid (compare Massot, Abstr., 1894, i, 356); on treatment with thionyl chloride, it yields the chloride,  $\text{CMe}_2\text{:CHBr}\cdot\text{COCl}$ , which has b. p. 178° or 73°/16 mm., and when heated in ethyl acetate solution with zinc gives brown, amorphous products; the anilide,



has m. p. 90°.

Benzylidenemalonyl chloride, prepared by the action of phosphorus pentachloride on the corresponding acid in the presence of light petroleum, crystallises in white needles, m. p. 37°. It yields with pyridine an additive compound,  $\text{C}_{20}\text{H}_{16}\text{O}_2\text{N}_2\text{Cl}_2$ , which forms a pale yellow powder, m. p. 95—100° (decomp.).

Attempts to prepare benzylidenemalonic anhydride by the action of silver oxide on the chloride in ethereal solution yielded ethyl benzylidenemalonate.

F. B.

**Addition of Hydrogen Cyanide to Unsaturated Compounds.** PHILIP H. COBB (*Amer. Chem. J.*, 1911, 45, 604—605).—

During the course of some work on phenylmaleic and phenylfumamic acids, it was found that when an alcoholic solution of ethyl phenylpropionate is treated with an aqueous solution of potassium cyanide and the mixture boiled for some hours on the water-bath, potassium carbonate and phenylsuccinonitrile are produced in accordance with the equation:

$\text{CPh:}\dot{\text{C}}\cdot\text{CO}_2\text{Et} + 2\text{KCN} + 2\text{H}_2\text{O} = \text{CN}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CN} + \text{K}_2\text{CO}_3 + \text{EtOH}.$

This reaction is being extended to other unsaturated compounds.

E. G.

**Esters of Boric Acid.** GEORG COHN (*Pharm. Zentr.-h.*, 1911, 52, 479—485).—Esters of boric acid can be readily prepared by treating the acid with an excess of the alcohol in presence of hydrogen chloride or of sulphuric acid. A large excess of alcohol (five or six times the weight of boric acid) gives the best yield, and sulphuric acid is preferable to hydrogen chloride. In this way the methyl, ethyl, propyl, and isobutyl esters have been prepared.

Attempts to employ these esters for the alkylation of bases, phenols, and acids were unsuccessful, except in the case of salicylic acid, which, when boiled for a long time with methyl borate, yielded methyl salicylate quantitatively. *p*-Hydroxybenzoic acid remains unchanged under these conditions, and no reaction was observed with aniline, dimethylaniline, phenol, or resorcinol.

Aromatic hydroxy-acids react readily with boric esters, yielding substances of the type of trisalicylboric acid,  $\text{B}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_3$ , which

is formed initially in the above-mentioned esterification. The compound crystallises in long prisms, which on heating begin to sinter at about 230°, and are completely melted (with energetic decomp.) at 260–270°. When trisalcylboric acid is boiled with phenylhydrazine, a substance, m. p. 223°, is obtained, which crystallises in light brown laminae, and reduces copper sulphate even in the cold. *m*- and *p*-Hydroxybenzoic acids do not give analogous compounds. *Tri-o*-hydroxytoluoylboric acid sinters at 220°, and has m. p. 245–247° (decomp.). *Tri-m*-hydroxytoluoylboric acid sinters at 175°, but melts sharply at 261° (decomp.). *Tri-p*-hydroxytoluoylboric acid sinters at 143°, and has m. p. 210–212° if slowly heated; if plunged into a bath at 155° the substance froths up, crystallises, and melts then at 210–212°.

*Tri-α*-hydrozynaphthoylboric acid sinters at 250°, m. p. 255° (decomp.). *Tri-β*-hydrozynaphthoylboric acid is still solid at 263°.

*Trisresorcinoylboric acid* (from carefully dried resorcinic acid) becomes yellow at 220°, but suffers no further change below 260°.

Gallie acid does not react. Tartaric acid and methyl or ethyl borate yield a small quantity of a white, crystalline substance.

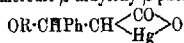
Salicylamide and boric ester yield a white, crystalline substance, which begins to sinter at 220°, and melts at about 265°. The analyses indicate the composition  $B(O\cdot C_6H_4\cdot CO\cdot NH_2)_3$ . R. V. S.

**Ketens. XXII. Attempts to Prepare *o*-Methoxyphenylketen.** HERMANN STAUDINGER and OTTO KUPFER (*Ber.*, 1911, 44, 1633–1640).—Attempts to remove hydrogen chloride from phenylmethoxyacetyl chloride by means of tripropylamine, with the formation of phenylmethoxyketen, proved fruitless.

*o*-Methoxyphenylacetyl chloride,  $OMe\cdot CHPh\cdot COCl$ , prepared by the action of thionyl chloride on the corresponding acid, is a colourless liquid, b. p. 80–81°/0.1 mm. At temperatures above 120°, it decomposes into carbon monoxide, methyl chloride, and benzaldehyde.

F. B.

**Ether Derivatives of *β*-Phenylhydracrylic Acid (*β*-Hydroxy-*β*-phenylpropionic Acid).** WALTHER SCHRAUTH, WALTER SCHÖLLE, and RICHARD STRUENSEE (*Ber.*, 1911, 44, 1432–1436).—The anhydrides of *α*-hydroxymercuri-*β*-alkyloxy-*β*-phenylpropionic acids,



(this vol. i, 595), when hydrolysed with mineral acids are completely decomposed, yielding cinnamic acids, and when the esters of the *α*-acetoxymercuri-*β*-alkyloxy-*β*-phenylpropionic acids are treated with an alcoholic solution of hydrogen sulphide, esters of cinnamic acid are formed. By using an alcoholic solution of ammonium sulphide the esters of the mercuriacetate derivatives can be transformed into esters of *β*-alkyloxy-*β*-phenylpropionic acids. The corresponding acids can be obtained by hydrolysing the esters or by the action of hydrogen sulphide on solutions of the anhydrocompounds in dilute sodium hydroxide.

*Methyl β*-methoxy-*β*-phenylpropionate,  $OMe\cdot CHPh\cdot CH_2\cdot CO_2Me$ , pre-

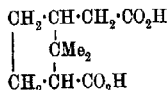


pared from the methyl  $\alpha$ -acetoxymercuri- $\beta$ -methoxy- $\beta$ -phenylpropionate, is an oil with b. p.  $253^\circ$  (corr.), and the corresponding acid,  $C_{10}H_{10}O_3$ , crystallises from light petroleum in stout, colourless plates, m. p.  $98^\circ$ .

*Methyl  $\beta$ -ethoxy- $\beta$ -phenylpropionate*,  $OEt\cdot CHPh\cdot CH_2\cdot CO_2Me$ , is a colourless oil with an unpleasant odour, and has b. p.  $256^\circ$  (corr.). The corresponding acid,  $C_{11}H_{14}O_3$ , crystallises from light petroleum in colourless plates, m. p.  $75^\circ$ , and when boiled for a short time with hydrochloric acid yields cinnamic acid.

*$\beta$ -Propoxy- $\beta$ -phenylpropionic acid*,  $OPr\cdot CHPh\cdot CH_2\cdot CO_2H$ , crystallises from water in colourless plates, m. p.  $59^\circ$ , and the corresponding isopropoxy-acid from light petroleum in plates, m. p.  $73^\circ$ .  *$\beta$ -isobutoxy- $\beta$ -phenylpropionic acid*,  $C_{13}H_{18}O_3$ , has m. p.  $67.5^\circ$ . J. J. S.

**Complete Synthesis of Pinophanic Acid and the Constitution of Ketopinic and Tricyclic Acid.** GUSTAV KOMPPA (Ber., 1911, 44, 1536—1541).—The homoapocamphoric acid (annexed



formula), prepared by reduction of apocamphoric anhydride to apocampholide, addition of potassium cyanide to this, and hydrolysis, is identical with pinophanic acid (Gilles and Rennick, Proc., 1897, 13, 65), but not with camphenecamphoric acid. Accordingly, ketopinic acid, from which pinophanic acid is obtained by heating with alkali or with sodium ethoxide, has the annexed formula, and not that suggested by Bredt and May. It follows, further, from this that tricyclic [dehydrocamphenylic] acid has the constitution suggested by Semmler and by Komppa and Hintikka (Abstr., 1908, i, 852), which readily explains the conversion into ketopinic acid.

The corresponding cyclic ketone has been obtained from homoapocamphoric acid in small quantities; the semicarbazone has m. p.  $209$ — $211^\circ$ , and the ketone is probably identical with fenchocamphorone.

dl-apoCampholide, obtained by reducing apocamphoric anhydride, crystallises in long, indefinite, feathery masses or short, thick, triclinic prisms, m. p.  $164^\circ$ . When kept with hydrogen bromide in acetic acid, bromoapocampholic acid,  $CH_2Br\cdot C_7H_{12}\cdot CO_2H$ , is obtained, crystallising in aggregates of indefinite crystals, m. p.  $139^\circ$ .

Cyanoapocampholic acid, prepared by heating apocampholide with potassium cyanide, forms short, many-faced, but indefinite crystals, m. p.  $141.5$ — $142^\circ$  (corr.). On hydrolysis, homoapocamphoric acid is obtained in rhombic plates, m. p.  $203$ — $204^\circ$ , in every way identical with pinophanic acid prepared from ketopinic acid. The diamide crystallises in slender needles, m. p.  $194$ — $195^\circ$ . E. F. A.

**Action of Benzoyl Chloride and Potassium Cyanide on Benzoyloxybenzoic Acids and on Acylated Hydroxybenzoyloxybenzoic Acids.** FRANCIS E. FRANCIS and MAX NIERENSTEIN (Annalen, 1911, 382, 194—210. Compare Francis and Davis, Trans., 1909, 95, 1404; Davis, *ibid.*, 1910, 96, 949).—By the action of

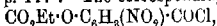
benzoyl chloride and potassium cyanide on hydroxybenzoyloxybenzoic acids, it was thought that acids of the type of galloylgallic acid (digallic acid), that is, compounds of the depside type (Fischer and Freudenberg, Abstr., 1910, i, 266), might be produced according to the equation:

$$OAc \cdot R \cdot CO \cdot O \cdot R' \cdot CO_2H + PhCO \cdot Cl + KCN =$$

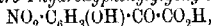

The reaction takes place when the nucleus contains negative substituents, for example, 3-*m*-nitrobenzoyloxybenzoic acid, 4-*m*-nitrobenzoyloxybenzoic acid, 4-*m*-nitro-*p*-ethylcarbonatobenzoyloxybenzoic acid, diethylcarbonatoprotocatechuyl-*o*-nitrosalicylic acid, 4-nitro-2-*p*-ethylcarbonatobenzoyloxybenzoic acid, and penta-acetylgalloylgallic acid, but not with the following acids: 4-benzoyloxybenzoic acid, 4-*p*-ethylcarbonatobenzoyloxybenzoic acid and the corresponding 3-oxy-acid, 4-*mp*-diethylcarbonatobenzoyloxybenzoic acid, and 3-nitro-4-dimethylcarbonatobenzoyloxybenzoic acid.

3-*m*-Nitrobenzoyloxybenzoic acid,  $NO_2 \cdot C_6H_4 \cdot CO \cdot O \cdot C_6H_4 \cdot CO_2H$ , obtained by the action of *m*-nitrobenzoyl chloride on *m*-hydroxybenzoic acid at 40° in the presence of 10% sodium hydroxide solution, crystallises from dilute alcohol in stout needles, m. p. 241°. The isomeric 4-*m*-nitrobenzoyloxybenzoic acid crystallises from methyl alcohol in long needles, m. p. 273—274° (decomp.). When shaken with benzoyl chloride and an aqueous solution of potassium cyanide, the two acids yield respectively *m*-benzoyloxybenzoic acid and *p*-benzoyloxybenzoic acid together with *m*-nitrobenzoylformic acid (Claisen and Thompson, Abstr., 1880, 253).

3-Nitro-4-ethylcarbonatobenzoic acid,  $CO_2Et \cdot O \cdot C_6H_3(NO_2) \cdot CO_2H$ , prepared from 3-nitro-4-hydroxybenzoic acid, ethyl chlorocarbonate, and *N*-sodium hydroxide solution, crystallises from dilute alcohol in stellate masses of needles, m. p. 117°. The corresponding acid chloride,



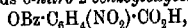
crystallises from a mixture of chloroform and light petroleum in long needles, m. p. 72°, and condenses with *p*-hydroxybenzoic acid in the presence of alkali, yielding 3-nitro-4-*p*-ethylcarbonatobenzoyloxybenzoic acid,  $CO_2Et \cdot O \cdot C_6H_3(NO_2) \cdot CO \cdot O \cdot C_6H_4 \cdot CO_2H$ , which crystallises from aqueous acetone in plates or from dilute alcohol in short, stout needles, m. p. 194—196° after beginning to sinter at 184°. Its decomposition into *m*-nitro-*p*-ethylcarbonatophenylglyoxylonitrile and *p*-benzoyloxybenzoic acid proceeds smoothly. The nitrile could not be isolated, but the crude oil when hydrolysed with concentrated hydrochloric acid gave 3-nitro-4-hydroxyphenylglyoxylic acid,



which crystallises from chloroform in glistening prisms, m. p. 61° after sintering at 59°.

3:4-Diethylcarbonatobenzoic acid,  $C_6H_3(O \cdot CO_2Et)_2 \cdot CO_2H$ , crystallises from dilute acetone in brilliant plates, m. p. 122—123° (decomp.); the corresponding chloride,  $C_{13}H_{18}O_4Cl$ , crystallises from a mixture of chloroform and light petroleum, has m. p. 55°, and reacts with *o*-nitrosalicylic acid in the presence of ether and dilute sodium hydroxide solution, yielding nitro-2-*mp*-diethylcarbonatobenzoyloxybenzoic acid,  $C_6H_3(O \cdot CO_2Et)_2 \cdot CO \cdot O \cdot C_6H_3(NO_2) \cdot CO_2H$ , which crystallises from dilute alcohol in brilliant, glistening needles, m. p. 212—214°.

(decomp.) when quickly heated. With benzoyl chloride and potassium cyanide solution it yields *o*-nitro-2-benzoyloxybenzoic acid,

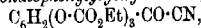


m. p. 117°, and a nitrile which on hydrolysis gave 3:4-dihydroxyphenylglyoxylic acid,  $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{CO} \cdot \text{CO}_2\text{H}$ . This acid crystallises from a mixture of chloroform and light petroleum in needles, m. p. 92°.

3:4-Diethylcarbonatophenylglyoxylonitrile,  $\text{C}_6\text{H}_3(\text{O} \cdot \text{CO}_2\text{Et})_2 \cdot \text{CO} \cdot \text{CN}$ , prepared from an ethereal solution of the corresponding chloride and an aqueous solution of potassium cyanide, crystallises from light petroleum in glistening needles, m. p. 38°. 4-Nitro-2-*p*-ethylcarbonatobenzoyloxybenzoic acid,  $\text{CO}_2\text{Et} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{CO}_2\text{H}$ , crystallises in small prisms, m. p. 194–196° (decomp.), and with benzyl chloride and potassium cyanide yields *p*-ethylcarbonatophenylglyoxylonitrile,  $\text{CO}_2\text{Et} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CN}$ , as small needles, m. p. 34°, and volatile under 10–12 mm. pressure. The nitrile when hydrolysed with concentrated hydrochloric acid yields *p*-hydroxyphenylglyoxylic acid,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CO}_2\text{H}$ , which crystallises from benzene in small cubes, m. p. 84°.

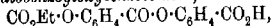
Penta-acetylgalloylgallic acid (Abstr., 1909, i, 402) reacts with benzoyl chloride and potassium cyanide, yielding 5-benzoyl-3:4-diacetyl gallic acid,  $\text{C}_6\text{H}_3(\text{O} \cdot \text{COPh})(\text{OAc})_2 \cdot \text{CO}_2\text{H}$ , which crystallises from methyl alcohol in small, pointed needles, m. p. 178–179°. The nitrile which was also formed when hydrolysed with concentrated hydrochloric acid gave galloylformic acid,  $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{CO} \cdot \text{CO}_2\text{H}$ , which crystallises from dilute alcohol in glistening needles, m. p. 114–116°. It gives the same coloration with ferric chloride as does gallic acid, but with potassium cyanide solution it gives a violet coloration.

3:4:5-Triethylcarbonatophenylglyoxylonitrile,

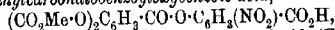


obtained from the corresponding chloride, crystallises from light petroleum in small, glistening needles, m. p. 98°.

3-*p*-Ethylcarbonatobenzoyloxybenzoic acid,

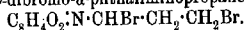


crystallises from dilute acetone in colourless needles, m. p. 148°, and 3-nitro-4-dimethylcarbonatobenzoyloxybenzoic acid,



prepared from 2:4-dimethylcarbonatobenzoyl chloride (Fischer, Abstr., 1909, i, 162) and *m*-nitro-*p*-hydroxybenzoic acid, crystallises from alcohol in small needles, m. p. 172° (decomp.). J. J. S.

**Compounds of the Propane Series.** SIEGMUND GABRIEL (*Ber.*, 1911, 44, 1905–1915. Compare Hildesheimer, Abstr., 1910, i, 891). —Hildesheimer (*loc. cit.*) has described the compound obtained by the action of red phosphorus and bromine on  $\alpha$ -phthaliminobutyric acid as  $\alpha\beta$ -dibromo- $\alpha$ -phthaliminopropane. A compound of this constitution has now been prepared independently, and found not to be identical with Hildesheimer's compound, which, accordingly, must have the composition of an  $\alpha\gamma$ -dibromo- $\alpha$ -phthaliminopropane,



By the action of bromine on phthaliminoacetone, mono-, di-, tri-, and tetra-bromo-derivatives have been obtained.

*Phthaliminobromoacetone*,  $C_8H_5O_2 \cdot N \cdot CH_2 \cdot CO \cdot CH_2Br$ , prepared either by the action of phosphorus pentabromide or of bromine in chloroform solution on phthaliminoacetone, crystallises in colourless, slender, matted needles, m. p. 147—148°. When fused with potassium phthalimide, diphtaliminoacetone is obtained, proving the position of the bromine atom, whilst on heating with sodium acetate at 170°, *phthalimino-hydroxyacetone*, crystallising in needles of silky lustre, m. p. 141—142°, is formed.

On hydrolysis of phthaliminobromoacetone by boiling with water, phthalimide and methylglyoxal are the main products.

*Phthaliminodibromoacetone*,  $C_8H_5O_2 \cdot N \cdot CHBr \cdot CO \cdot CH_2Br$ , produced on bromination in benzene solution or further bromination of the monobromo-compound, forms long needles, m. p. 126—127°. On hydrolysis, phthalimide and bromomethylglyoxal are obtained.

*Phthaliminotribromoacetone*,  $C_8H_5O_2 \cdot N \cdot CHBr \cdot CO \cdot CHBr_2$ , crystallises in obliquely-cut rods, m. p. 146—147°. On hydrolysis phthalimide and dibromomethylglyoxal are obtained, the latter being identified as the phenylhydrazone, crystallising in citron-yellow needles, m. p. 174°—175°.

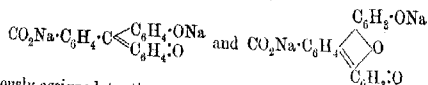
*Phthaliminotetabromoacetone*,  $C_8H_5O_2 \cdot N \cdot CHBr \cdot CO \cdot CBr_3$ , crystallises in rhombic plates, m. p. 153—154°. On hydrolysis bromoform is obtained.

On distillation of phthalimino-*n*-butyrylchloride, propenylphthalimide, m. p. 151°, is obtained (compare Johnson and Jones, this vol., i, 455).

The isomeric *phthaliminocyclopropane*,  $C_8H_5O_2 \cdot N \cdot CH \cdot \begin{smallmatrix} CH_2 \\ | \\ CH_2 \end{smallmatrix}$ , prepared from aminocyclopropane and phthalic acid, forms colourless, rhombic plates, m. p. 135—136°. It does not form an additive compound with bromine.

Propenylphthalimide combines with bromine in chloroform solution, forming *phthalimino- $\alpha\beta$ -dibromopropane*,  $C_8H_5O_2 \cdot N \cdot CHBr \cdot CHBr \cdot CH_3$ , which crystallises in flat, hexagonal crystals, m. p. 105—106°, and differs from Hildesheimer's compound (*loc. cit.*), m. p. 147°. On hydrolysis, phthalimide and acetylcarbinol are obtained. E. F. A.

**Composition of Phthalein Salts.** RICHARD MEYER and FERD. POSNER (*Ber.*, 1911, 44, 1954—1957).—The authors have carefully re-investigated the composition of the red sodium salt of phenolphthalein and the violet sodium salt of hydroquinonephthalein, and obtain results which are in agreement with the formulæ:



previously assigned to these compounds (Meyer and Spengler, *Abstr.*, 1905, i, 440; compare Baeyer, *Abstr.*, 1910, i, 219; Kehrman, *ibid.*, 406).

The calcium salt of phenolphthalein is obtained crystalline by shaking phenolphthalein with water and calcium hydroxide at the ordinary temperature, and heating the resulting solution to boiling. It has the composition  $C_{20}H_{12}O_4Ca \cdot 1\frac{1}{2}H_2O$ , and forms reddish-brown, flat

prisms with a green lustre; the anhydrous salt has a metallic green colour (compare D.R.-P. 223969).

F. B.

**By-products of the Preparation of Ethyl Phloroglucinol-dicarboxylate.** HERMANN LEUCHS and FRITZ SIMION (*Ber.*, 1911, 44, 1874—1884. Compare Leuchs and Geserick, *Abstr.*, 1903, i, 106).—In the preparation of ethyl phloroglucinol dicarboxylate by the Baeyer synthesis, ethyl malonate and ethyl acetate are present in the reaction mixture, and there is the possibility of 3 mols. of acetate uniting to form phloroglucinol, or of 3 mols. of malonate uniting to form a tricarboxylate, or of the formation of phloroglucinolmonocarboxylate from 2 mols. of acetate and 1 mol. of malonate. The by-products of the reaction have been examined from this point of view, and five such isolated, namely, an *ester*,  $C_{17}H_{20}O_{10}$ , m. p.  $96^{\circ}$ , an *acid*,  $C_{15}H_{16}O_{10}$ , and an *ester*,  $C_{14}H_{16}O_8$ , both derived from this by secondary changes, a compound,  $C_{25}H_{30}O_{12}$ , and a compound,  $C_{15}H_{18}O_{11}$ , formed by the combination of 4 mols. of ethyl malonate.

Neither phloroglucinol-mono- nor -tri-carboxylate is formed, although the latter may represent an intermediate stage in the formation of some of the compounds mentioned. More probably the molecules are first united in chains, and the closing of the ring takes place subsequently.

The *ester*,  $C_{17}H_{20}O_{10}$ , has been more fully investigated. With hydroxylamine, an isooxazolone,  $\begin{matrix} N \\ | \\ CR \cdot CH_2 \end{matrix} > \begin{matrix} O \\ | \\ CO \end{matrix}$ , is formed. With concentrated nitric acid, the side-chain is hydrolysed, and the *ester*,  $C_{11}H_{16}O_8$ , formed.

On acetylation, a *triacetate* is formed, water being at the same time eliminated. On complete hydrolysis with hydrogen iodide, an *acid*,  $C_9H_6O_5$ , is obtained. Cold sodium hydroxide eliminates a molecule of alcohol.

The formula attached is applied to the *ester*  $C_{17}H_{20}O_{10}$  to express this behaviour:  $CO_2Et \cdot CH < \begin{matrix} CO \\ | \end{matrix} \begin{matrix} CH(CO_2Et) \\ | \end{matrix} > CO$   
 $CO \cdot CH(CO \cdot CH_2 \cdot CO_2Et) > CO$ .

It crystallises in long, matted, colourless needles, m. p.  $95.5-96.5^{\circ}$ , and shows a deep reddish-brown coloration with ferric chloride.

The isooxazolone,  $C_{15}H_{12}O_6N$ , produced on boiling with hydroxylamine, forms four-sided, glistening tablets or prisms, m. p.  $203-204^{\circ}$  (decomp.).

The *acetate*,  $C_{25}H_{30}O_{12}$ , crystallises in yellow, dome-like prisms, m. p.  $109-110^{\circ}$ . The mother liquors contain the *sodium* salt, four-sided, yellow plates, m. p.  $260^{\circ}$  (decomp.), of an *ester*,  $C_{21}H_{26}O_{12}$ , or  $C_{19}H_{18}O_{11}$ , which crystallises in needles, m. p.  $145-146^{\circ}$ . By the action of hydrogen iodide on the acetate, an *acid*,  $C_9H_6O_5$ , crystallising in feathery needles, is obtained, m. p. above  $300^{\circ}$ .

The *anhydride*,  $C_{17}H_{18}O_9$ , of the *ester*,  $C_{17}H_{20}O_{10}$ , crystallises in long, hexagonal needles, m. p.  $153-154^{\circ}$ .

With the *ester*, sodium hydroxide gives a product,  $C_{15}H_{14}O_9$ , crystallising in massive prisms, m. p.  $162-163^{\circ}$ .

Concentrated nitric acid forms from the *ester*, glistening, broad needles, m. p.  $128-129^{\circ}$ , of the *compound*,  $C_{14}H_{16}O_8$ , identical with

that formed during the original condensation. A second product,  $C_{16}H_{18}O_{10}$ , crystallises in needles or prisms, m. p. 99—100°.

The condensation product,  $C_{18}H_{16}O_{10}$ , consists of colourless, glistening, obliquely-cut prisms, m. p. 165° (decomp.). When fused, it forms the compound,  $C_{14}H_{16}O_8$ , just described.

The by-product,  $C_{22}H_{20}O_{12}$ , forms pale yellow needles, m. p. 196—197°.

The fifth condensation product, the ester,  $C_{18}H_{18}O_{11}$ , crystallises in yellow, pointed, four-sided plates, m. p. 177—178°, and is identical with a substance isolated by Willstätter (Abstr., 1899, i, 577). It yields phloroglucinol when fused with potassium hydroxide, and is considered to be formed by the condensation of 4 mols. of ethyl malonate.

E. F. A.

**Synthesis of Glucovanillic Acid and of Gluco-*p*-hydroxybenzoic Acid.** FERDINAND MAUTHNER (*J. pr. Chem.*, 1911, [ii], 83, 556—560. Compare Abstr., 1910, i, 677).—*Methyl tetra-acetylglucovanillate*,  $C_{22}H_{28}O_{13}$ , m. p. 144—145°, obtained by shaking a solution of methyl vanillate in dilute sodium hydroxide with ethereal  $\beta$ -acetobromoglucose for twenty-six hours, is hydrolysed by aqueous barium hydroxide at the ordinary temperature, yielding Tiemann and Reimer's glucovanillic acid.

In a similar manner, methyl *p*-hydroxybenzoate and  $\beta$ -acetobromoglucose yield *methyl tetra-acetylgluco-p-hydroxybenzoate*,  $C_{22}H_{26}O_{12}$ , m. p. 159—160°, which is converted into *gluco-p-hydroxybenzoic acid*,  $C_{13}H_{10}O_8$ , m. p. 211—212°, by shaking with 6% barium hydroxide for twenty-four hours at the ordinary temperature.

C. S.

**Chemical Action of Light.** XXI. GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1911, 44, 1558—1564).—By the action of light on benzaldehyde a *trimeride*, m. p. 144—145°, is obtained, isomeric with that of Mascarelli, m. p. 247—248°, which is also formed in this reaction. The new polymeride crystallises in chalk-white, micro-crystalline crusts, and does not combine with semicarbazide. Cinnamaldehyde after a year's exposure to light gives a reddish-brown, transparent resin, which after purification forms an almost colourless powder, m. p. 115°; this is probably a *polymeride* of four or five molecules.

A mixture of benzophenone and benzaldehyde when exposed to light forms a compound,  $C_{27}H_{20}O_3$ , composed of two molecules of benzaldehyde and one of benzophenone. This crystallises in colourless, voluminous needles, m. p. 245°.

A mixture of benzophenone and diethyl dihydrocollidindicarboxylate in benzene yields after a year's exposure a mixture of benzopinacene and ethyl collidinedicarboxylate. The *picrate* of the latter forms large, yellow needles, m. p. 164°; the *aurichloride* is oily, and the *platinichloride* yields orange-red platelets, m. p. 181°.

Quinaldine and acetone unite to a condensation product,  $C_{23}H_{22}N_2$ , composed of 2 mols. of quinaldine and 1 mol. of acetone, which crystallises in light yellow, slender needles, m. p. 212°. It is a diacid base; on the addition of hydrochloric acid it becomes orange-red, but on stirring

the solution becomes colourless. When this is evaporated a barely yellow-coloured residue is obtained, which immediately becomes orange-red on the addition of water.

The *dihydrochloride* is colourless; the *monohydrochloride* is orange-red, m. p. 270°. The *platinichloride* is orange-red; the *aurichloride* is at first a golden-yellow, crystalline precipitate, but with water a brown mass is obtained and the filtrate is violet-brown. E. F. A.

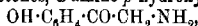
**Rate of Transformation of *syn*- into *anti*-Oximes.** THOMAS S. PATTERSON and ANDREW McMILLAN (*Proc. Phil. Soc. Glasgow*, 1911, Reprint 7 pp.).—In continuation of previous work (*Trans.*, 1907, 91, 504; 1908, 83, 1042), the authors have determined the velocity of transformation of a number of substituted benzsynaldoximes into the *anti*-forms in ethyl tartrate solution.

The following are the mean values for 1000 *k* at 26°: Benzsynaldoxime, 6.38; *p*-tolylsynaldoxime, 5.18; anisysynaldoxime, 6.82; piperonsynaldoxime, 3.59; *o*-nitrobenzsynaldoxime, 1.10; *m*-nitrobenzsynaldoxime, 4.16; *p*-iodobenzsynaldoxime, 5.335.

In the case of *p*-nitrobenzsynaldoxime the transformation into the *anti*-oxime takes place so rapidly that no measurements of the rate of change could be made. F. B.

**Synthesis of  $\alpha$ -Amino-ketones by means of Hexamethylenetetramine.** CARL MANNICH and FRIEDRICH L. HAHN (*Ber.*, 1911, 44, 1542—1552).—A large number of  $\alpha$ -halogen ketones readily form crystalline additive products with hexamethylenetetramine, iodides reacting more readily than bromides or chlorides. These compounds are colourless, soluble salts, which tend to decompose when crystallised and decompose also on warming. When hydrolysed with a large excess of alcohol and 38% hydrochloric acid, the corresponding amines are obtained, but the reaction is complicated by the formation of condensation products with the formaldehyde derived from hexamethylenetetramine. In the case of those bases which are stable in the free state, the formaldehyde can be fixed by adding sodium hydrogen sulphite.

Two of the amino-ketones,  $\omega$ -amino-*p*-hydroxyacetophenone,



and aminoacetylcatechol,  $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NH}_2$ , were obtained as free bases, although  $\alpha$ -amino-ketones usually condense to form dihydropyrazines. The condensation is possibly hindered by the phenolic nature of the compounds, or more probably it depends on the solubility of the amino-ketones. When they are sparingly soluble, condensation does not take place.

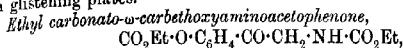
$\omega$ -Chloroacetophenone and hexamethylenetetramine form a salt-like additive product, m. p. 145°. The similar compound from  $\omega$ -bromoacetophenone and hexamethylenetetramine has m. p. 165°. Either product on treatment for three days with hydrochloric acid and alcohol gives the *hydrochloride of aminoacetophenone*, m. p. 186–187°; the *hydrobromide* has m. p. 217–218° (decomp.).

$\omega$ -Carbethoxyaminoacetophenone,  $\text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO}_2\text{Et}$ , prepared by the interaction of the aminoacetophenone salts with ethyl chloro-

carboxylate, crystallises in slender needles, m. p. 58°. It is reduced by sodium amalgam and alcohol to *ω*-carbethoxyaminomethylphenylcarbinol, which crystallises in colourless plates, m. p. 86°.

*ω*-Chloro-*p*-methoxyacetophenone and hexamethylenetetramine condense to a product, m. p. 170°, which is decomposed into *ω*-amino-*p*-methoxyacetophenone hydrochloride, m. p. 197° (decomp.); this becomes red in solution on the addition of ammonia, and orange needles of a dihydropyrazine separate.

*ω*-Amino-*p*-hydroxyacetophenone hydrochloride crystallises in colourless platelets, m. p. 242° (decomp.). The free base is stable, crystallising in glistening plates.



forms slender, colourless plates, m. p. 85–86°.

*ω*-Chloroacetylcatechol, m. p. 173°, is best prepared by heating equal quantities of catechol, chloroacetic acid, and phosphoryl chloride in a large flask on the water-bath until the liberation of hydrogen chloride ceases. The diacetate has m. p. 110–111°, but the additive product with hexamethylenetetramine could not be obtained pure.

*ω*-Iodoacetylcatechol diacetate, obtained by interaction of the chloride with sodium iodide, has m. p. 110–111°; it forms a hexamethylenetetramine additive product, m. p. 171°.

*ω*-Aminoacetylcatechol is a heavy powder, decomp. above 200°; the hydrochloride crystallises in lustrous plates, which become brown at 230°, m. p. 252° to a dark red liquid.

*ω*-Bromoacetoveratrone,  $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CO}\cdot\text{CH}_2\text{Br}$ , obtained by bromination of acetoveratrone in chloroform, has m. p. 80–81°; the additive product with hexamethylenetetramine crystallises in needles.

*ω*-Aminoacetoveratrone hydrochloride forms colourless, lustrous needles, m. p. 221°.

*ω*-Chloroacetylpyrogallol triacetate,  $\text{C}_6\text{H}_2(\text{OAc})_3\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ , has m. p. 100–101°. When oxidised with potassium permanganate in acetone, an acid containing acetyl is obtained, which is hydrolysed to pyrogallolcarboxylic acid, thus proving the positions 1, 2, 3, 4 for the substituting groups in chloroacetylpyrogallol. The triacetate does not combine with hexamethylenetetramine.

*ω*-Iodoacetylpyrogallol triacetate has m. p. 139–140°; it forms an additive product with hexamethylenetetramine, m. p. 130°, but *ω*-aminoacetylpyrogallol could not be obtained from this.

Acetylpyrogallol trimethyl ether has b. p. 165°/12 mm., m. p. 14–15°. Bromoacetylpyrogallol trimethyl ether is a viscid oil, m. p. 174–176°, forming colourless crystals, m. p. 50–51°; it does not form a hexamethylenetetramine additive compound. E. F. A.

Isolation of an Enolic Dibromide and the Course of the Reaction in the Bromination of Acetophenone and Similar Ketones. FRIEDRICH L. HAHN (*Ber.*, 1911, 44, 1552–1553).—When bromine is passed into a well cooled solution of acetoveratrone in a little chloroform or ether, a yellowish-red dibromide,  $\text{C}_{10}\text{H}_{12}\text{O}_3\text{Br}_2$ , separates. This is very unstable, and decomposes completely within



twelve hours. When covered with ether and well shaken with dilute sodium hydroxide, both layers remain colourless; the ether on evaporation yields  $\omega$ -bromoacetoveratrone, an indication that the ketone reacts in the enolic form, and that the dibromide has the formula  $C_6H_3(OMe)_2 \cdot CBr(OH) \cdot CH_2Br$ .

When acetophenone is brominated in ice-cold chloroform solution, no hydrogen bromide is liberated, neither does the brownish-red solution contain free bromine until at least 1 mol. of bromine for each mol. of ketone has been added. Only on warming or shaking with water is hydrogen bromide liberated, and the solution becomes lighter in colour; it then contains  $\omega$ -bromoacetophenone. If bromination is performed in a solution of sodium acetate in acetic acid, bromine is not fixed, even at the temperature of the water-bath, so long as no enol is present. On the addition of concentrated hydrochloric acid a trace of enol is formed and a violent reaction sets in, the solution being immediately decolorised.

E. F. A.

**Chemical Action of Light. XX.** GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1911, **44**, 1554—1558. Compare *ibid.*, 1901, **34**, 1541).—By the action of light on a mixture of acetone (1 vol.) and ethyl ether (2 vols.) there are formed isopropyl alcohol, an additive product of acetone and ether,  $C_7H_{10}O_2$ , b. p. 138—141°, probably the *monoethyl ether of  $\beta$ -methylbutylene  $\beta$ -glycol*, and a product,  $C_{11}H_{22}O_3$  or  $C_{11}H_{24}O_3$ , b. p. 109—112°/20 mm.

Acetophenone and ethyl ether after seven months' exposure to light yield an additive product,  $C_{12}H_{18}O_2$ , b. p. 247°, together with a further condensation product.

Benzophenone and ethyl ether form benzopinacolone and an additive product,  $C_{17}H_{20}O_2$ , crystallising in colourless prisms, m. p. 51°, and stable towards permanganate; it has probably the composition  $OH \cdot CPh_2 \cdot CHMe \cdot OEt$ . A more complicated condensation product is also obtained.

E. F. A.

**Ketens. XIX. Formation and Preparation of Diphenylketen.** HERMANN STAUDINGER (*Ber.*, 1911, **44**, 1619—1623).—Diphenylketen is formed in almost quantitative yield by the interaction of equal molecular quantities of diphenylacetyl chloride and tripropylamine in ethereal solution. It is also obtained, together with  $\omega$ -chlorodiphenylmethane and tetraphenylethylene, when diphenylacetyl chloride is distilled in a current of carbon monoxide under ordinary pressure. It is, however, best prepared by allowing a benzene solution of azibenzil to flow slowly into a flask heated at 100°, and distilling the resulting diphenylketen under diminished pressure (compare Schroeter, *Abstr.*, 1909, **i**, 617).

The residue from the distillation separates from glacial acetic acid in yellow crystals of the composition  $C_{28}H_{20}O_2N_2$ , m. p. 201°, and consists of an additive compound of diphenylketen with azibenzil.

F. B.

**Beckmann Transformation.** FERDINAND HENRICH (*Ber.*, 1911, **44**, 1533—1536. Compare Schroeter, this vol., **i**, 505).—When

etheral solutions of the *syn*-modifications of dypnoneoxime (Abstr., 1904, i, 431) and of benzylideneacetophenoneoxime (Abstr., 1907, i, 324) are subjected to the Beckmann transformation by phosphorus pentachloride, white substances are first precipitated, which are then converted by the further addition of phosphorus pentachloride into the yellow products, from which the anilides are finally obtained by the action of water. Similar behaviour is exhibited by pivalophenoneoxime (Schroeter, *loc. cit.*) and by benzophenoneoxime. These white substances are shown to be the *hydrochlorides* of the oximes, since they are produced by passing hydrogen chloride into ethereal solutions of the *syn*-oximes, and regenerate the oximes by treatment with cold aqueous sodium carbonate. It seems, therefore, that an oxime undergoes the Beckmann transformation only when it has basic (unsaturated) properties. The *anti*-oximes of the preceding substances, which do not undergo the Beckmann transformation, likewise do not have pronounced basic (unsaturated) properties. C. S.

**Isomerism and Isomorphism of the Yellow and the Red Fluorenones.** HANS STOBBE (*Ber.*, 1911, 44, 1481—1488).—Kerp's statement that the red and the yellow modifications of fluorenone (diphenylene ketone) are true isomerides (Abstr., 1896, i, 238) is confirmed by the author, who shows that the two substances differ, not only in the solid, but also in the liquid state and in solution.

The yellow ketone has m. p. 83—84°, and melts again at this temperature after resolidifying. The red ketone has m. p. 82—83°, but after resolidifying has m. p. 83—84°. Mixtures of the two ketones in any proportions have m. p. 83—84°. The fused mixture is orange, and solidifies in orange crystals. The red and the yellow, crystalline forms and also the orange mixed crystals are all isomorphous, crystallising in rhombic plates, more rarely in flattened needles. The red ketone crystallises from light petroleum in the dark, at first in blood-red, short crystals, but after repeated crystallisation in orange crystals which get paler in colour and more elongated, indicating a gradual conversion of the red into the yellow form. The conversion is readily accomplished by cold concentrated sulphuric acid.

The absorption spectra of the two modifications in alcohol, both in the visible and in the ultra-violet regions, have been measured. The latter are identical, the former, of course, are different. The optical behaviour leads the author to the opinion that Kerp's constitutions for the two ketones (*loc. cit.*) are untenable, and that the two substances furnish yet another instance of a pair of isomerides, the constitutions of which cannot be represented by present-day structural or stereochemical theories (compare Schaum, Abstr., 1910, i, 391).

C. S.

**$\beta\zeta$ -Dibenzoyl- $\beta\zeta$ -dimethylheptane and *acac*-Tetramethyl-pimelic Acid.** ALBIN HALLER and EDOUARD BAUER (*Compt. rend.*, 1911, 152, 1638—1642).—The general method for preparing trialkyl derivatives of acetic acid (Abstr., 1909, i, 131) has been applied to the synthesis of dibasic acids.

The sodium derivative of phenyl isopropyl ketone, prepared by

means of sodamide, reacts with  $\alpha$ -dibromopropene, giving a small quantity of an unstable liquid, b. p.  $171-173^{\circ}/13$  mm., probably of the constitution  $\text{COPh}\cdot\text{CMe}_2\cdot[\text{CH}_2]_2\cdot\text{CH}_2\text{Br}$ ; the principal portion of the product, however, consists of  $\beta$ -*dibenzoyl*- $\beta$ -*dimethylheptane*,

$\text{COPh}\cdot\text{CMe}_2\cdot[\text{CH}_2]_5\cdot\text{CMe}_2\cdot\text{COPh}$ ,  
silky needles, m. p.  $48-49^{\circ}$ , b. p.  $250-255^{\circ}/15$  mm. This diketone forms a *dioxime*, m. p.  $223-224^{\circ}$ , and undergoes the usual scission when treated with sodamide, giving rise to *acac-tetramethylpimelic acid*, needles, m. p.  $191-192^{\circ}$ . *acac-Tetramethylpimelic acid*,  
 $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot[\text{CH}_2]_3\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ ,  
forms hard crystals, m. p.  $168-169^{\circ}$ .

The reaction follows the same course when  $\alpha$ -chloro- $\gamma$ -bromopropene is used instead of the dibromo-derivative.  $\epsilon$ -*Chloro*- $\beta$ -*benzoyl*- $\beta$ -*methylpentane*,  $\text{COPh}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ , has b. p.  $165^{\circ}/11$  mm.

W. O. W.

*o*-Dibenzoylbenzene and its Homologues. ALFRED GUYOT and F. VALLETTE (*Ann. Chim. Phys.*, 1911, [viii], 23, 363-397).—Guyot and Catel (Abstr., 1905, i, 226, 516, 540; 1906, i, 761; 1907, i, 76) have drawn attention to the analogy which exists between the reactions of *o*-dibenzoylbenzene and those of diphenylphthalide and phenyloxanthranol, and Haller, Guyot, and Pignet have shown that under certain conditions the phthaleins are capable of being isomerised into *o*-dibenzoylbenzene derivatives (Abstr., 1910, i, 285). The authors have therefore generalised the work of Guyot and Catel, and prepared a number of dibenzoylbenzene homologues.

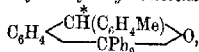
When magnesium phenyl bromide in ether reacts with excess of tolylphthalide, 2-hydroxy-2-phenyl-1-tolyl-1:2-dihydroisobenzofuran,  $\text{C}_6\text{H}_4\langle\text{CH}(\text{C}_6\text{H}_4\text{Me})\rangle_{\text{CPh}(\text{OH})}\text{O}$ , is formed. It is a colourless, crystalline powder, is very soluble in most organic solvents, and undergoes dehydration slowly at atmospheric temperature, but immediately and quantitatively on adding hydrochloric acid to its solution in alcohol, forming 2-phenyl-1-tolylisobenzofuran,  $\text{C}_6\text{H}_4\langle\text{C}(\text{C}_6\text{H}_4\text{Me})\rangle_{\text{CPh}}\text{O}$ , m. p.  $83^{\circ}$ ,

which crystallises in slender, yellow needles, gives yellow solutions showing a green fluorescence, of which the colour gradually disappears by the oxidation of the substance in air to *o*-toluoylbenzoylbenzene, m. p.  $139^{\circ}$ . This crystallises from a hot mixture of alcohol and benzene in small, brilliant prisms, dissolves in sulphuric acid with an intense magenta colour, and is recovered unchanged on addition of water. With hydrazine hydrate, it furnishes phenyltolylphthalazine,

$\text{C}_6\text{H}_4\langle\text{CPh}\rangle_{\text{C}(\text{C}_6\text{H}_4\text{Me})\cdot\text{N}}\text{N}$ , m. p.  $117^{\circ}$ , crystallising in small, colourless spangles. *o*-Benzhydriyltolhydriylbenzene,

$\text{OH}\cdot\text{CHPh}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4\text{Me}$ ,  
m. p.  $104^{\circ}$ , is obtained by the reduction of either hydroxyphenyltolyl-dihydroisobenzofuran or benzoyltoluoylbenzene with sodium amalgam in alcohol. It crystallises in thin, colourless spangles. Under similar conditions, phenyltolylisobenzofuran furnishes the 1:2-dihydrate, m. p.  $104^{\circ}$ , which crystallises in brilliant, colourless needles.

When, on the contrary, excess of magnesium phenyl bromide in ether is added to tolylphthalide, the condensation goes a stage further, and *o*-tolylhydri(triphenyl)carbinol,  $\text{HO}\cdot\text{CPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4\text{Me}$ , m. p.  $182^\circ$ , small crystals, is formed. This, on treatment with warm sulphuric acid, loses 2 mols. of water and gives 10-phenyl-9-tolyl-anthracene, m. p.  $192^\circ$ , which crystallises in feebly yellow, bulky prisms, and fluoresces violet on solution in benzene. On oxidation with sodium dichromate, it yields 9:10-dihydroxy-10-phenyl-9-tolyl-dihydroanthracene, m. p.  $212^\circ$  (anhydrous), which crystallises with some alcohol in transparent needles, gives an indigo-blue coloration with sulphuric acid, and liberates iodine from potassium iodide. Its constitution is established by its synthesis from the ethyl ether of phenyloxanthranol by the action of magnesium tolyl bromide (compare Guyot and Staebeling, Abstr., 1905, i, 885). In acetic acid solution, *o*-tolylhydri(triphenyl)carbinol is dehydrated by hydrochloric acid, forming 2:2-diphenyl-1-tolyl-dihydroisobenzofuran,



m. p.  $123^\circ$ , which crystallises in small, colourless needles from alcohol, and on oxidation with sodium dichromate in acetic acid exchanges the  $\text{H}$  atom for a hydroxyl group; this *hydroxy*-compound has m. p.  $130^\circ$ , and crystallises from alcohol, ether, or benzene. Its constitution was established by its synthesis from diphenylphthalide by the action of magnesium tolyl bromide.

The action of magnesium *p*-tolyl bromide on tolylphthalide is analogous to that of magnesium phenyl bromide on this substance, and the following products were obtained by methods strictly analogous to those employed for the lower homologues described above.

2-Hydroxy-1:2-ditolyl-1:2-dihydroisobenzofuran forms small crystals, and on heating loses 1 mol. of water, forming 1:2-ditolylisobenzofuran, m. p.  $125^\circ$ , crystallising in long, yellow needles. Ditoluoylbenzene, m. p.  $184^\circ$ , forms colourless crystals, and gives an intense magenta colour with sulphuric acid (compare Bauer, Abstr., 1905, i, 210). Its monophenylhydrazone, m. p.  $171^\circ$ , forms small, brilliant yellow prisms. Ditolylphthalazine, m. p.  $221^\circ$ , crystallises from alcohol in long, slender needles. *o*-Ditolylhydri(benzene), m. p.  $118^\circ$ , forms small, colourless spangles. 1:2-Ditolyl-1:2-dihydroisobenzofuran, m. p.  $89^\circ$ , separates from methyl alcohol in slender, colourless needles.

Ditolyl-*o*-tolylhydri(triphenyl)carbinol,

$\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4\text{I}_4\cdot\text{C}(\text{C}_6\text{H}_4\text{Me})_2\cdot\text{OH}$ , m. p.  $138^\circ$ , forms small, brilliant prisms, and in contact with sulphuric acid loses 2 mols. of water, giving 9:10-*p*-ditolyl-2-methylanthracene, which crystallises in yellow prisms and fluoresces violet in benzene and its homologues. On oxidation it gives 9:10-dihydroxy-9:10-ditolyl-2-methyldihydroanthracene, m. p.  $207^\circ$  (anhydrous), which crystallises with some alcohol in brilliant prisms, gives an indigo-blue coloration with sulphuric acid, and liberates iodine from potassium iodide.

Magnesium  $\alpha$ -naphthyl bromide in ether reacts with phenyl-

phthalide, forming 2-hydroxy-1-phenyl-2-naphthyl-1:2-dihydroisobenzofuran. This was obtained as an oil, which, on oxidation, gave *o*-benzoylnaphthoylbenzene, m. p. 104°, in small, colourless crystals, *o*-Toluylnaphthoylbenzene, m. p. 144°, crystallising in small, colourless prisms, was obtained similarly from the condensation product of magnesium  $\alpha$ -naphthyl bromide and tolylphthalide. T. A. H.

**Quinhydrones.** WILHELM SIEGMUND (J. pr. Chem., 1911, [ii], 83, 553—555).—By the addition of a warm ethereal solution of the phenol to a warm solution of *p*-benzoquinone in petroleum, the following quinhydrones have been obtained:  $3C_6H_4O_2, 4C_6H_3(OH)_2$ , m. p. 78°, black needles, from *p*-benzoquinone (2 mols.) and pyrogallol (1 mol.);  $3C_6H_4O_2, 4C_6H_3(OH)_2$ , m. p. 164°, green needles, from *p*-benzoquinone (1 mol.) and hydroxyquinol (1 mol.);

$3C_6H_4O_2, 2C_6H_3(OH)_2$ , m. p. 103°, red crystals, from *p*-benzoquinone (4 mols.) and phloroglucinol (1 mol.);  $C_6H_4O_2, C_6H_3(OH)_2$ , from *p*-benzoquinone (1 mol.) and 2:3-dihydroxynaphthalene (1 mol.), separates initially in pale red leaflets, finally in garnet-red needles, both forms having m. p. 78—80° (compare Abstr., 1909, i, 109). C. S.

**Constitution of Quinhydrone-like Substances.** ANGELO KNOB (Ber., 1911, 44, 1503—1506).—Richter's conception of quinhydrones as oxonium compounds (this vol., i, 136) is inapplicable to the quinhydrones obtained by Haakh from quinones and hydrocarbons (Abstr., 1910, i, 48). The author selects several of Richter's examples and shows that the constitutions ascribed to them are at variance with their properties. A true imonium compound,

$NO_2 \cdot C_6H_4 \cdot O \cdot NH_2 \cdot C_6H_4 \cdot NH_2 \cdot O \cdot C_6H_4 \cdot NO_2$ , m. p. 59° (decomp.), has been prepared from quinoned-imine and *p*-nitrophenol in ether. It forms yellow crystals and lacks, therefore, the chief criterion of a quinhydrone, namely, an intense colour in comparison with those of its components. C. S.

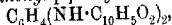
**Vat Dyes from  $\alpha$ -Naphthaquinone.** RUDOLF PUMMERER and KURT BRASS (Ber., 1911, 44, 1647—1656).—A number of substituted 2-amino- $\alpha$ -naphthaquinones have been prepared by the condensation of amino-compounds with  $\alpha$ -naphthaquinone. On reduction with alkaline hyposulphite, the majority of these compounds yield vats which dye cotton without a mordant. The dyes are, however, of no technical importance, partly on account of their lack of vivid shades, and partly because of their insufficient fastness to chlorine and light.

From experiments on the behaviour of several leuco-compounds of vat-dyes towards vegetable fibres, the authors draw the conclusion that the production of fast colours is determined by the following two factors: (1) the affinity of the leuco-compounds for the fibre, and (2) the firmness with which the dye is mechanically fixed on the fibre when the leuco-compound is oxidised.

2-*p*-Aminoanilino- $\alpha$ -naphthaquinone,  $\begin{matrix} C_6H_4 \cdot CO \\ CO-CH \end{matrix} \gg C \cdot NH \cdot C_6H_4 \cdot NH_2$ , obtained by reducing 2-*p*-nitroanilino- $\alpha$ -naphthaquinone with alkaline hyposulphite and oxidising the resulting solution with a current of air,

crystallises in dark violet prisms, m. p. 214° (not sharp); with strong sulphuric acid it gives a safranine-red solution, from which a yellowish-red sulphate is precipitated by water.

*N,N'-Di-2-α-naphthaquinonyl-p-phenylenediamine*,



is prepared by heating α-naphthaquinone with *p*-phenylenediamine in glacial acetic acid solution; it forms a brownish-violet, crystalline powder, m. p. 250° (not sharp), and gives with alkaline hyposulphite a light yellow vat, in which cotton is dyed brownish-violet. It is oxidised with lead peroxide in xylene solution, yielding probably *p*-benzoquinonedi-2-α-naphthaquinonyldi-imine.

2-(4')-Diphenylamino-α-naphthaquinone,  $\text{C}_{10}\text{H}_7\text{O}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_5\cdot\text{Ph}$ , obtained by heating α-naphthaquinone and 4-aminodiphenyl in alcoholic solution, crystallises in red needles, m. p. 215°.

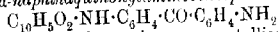
2-Benzidino-α-naphthaquinone,  $\text{C}_{10}\text{H}_7\text{O}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , prepared from benzidine and α-naphthaquinone, crystallises in brown needles, m. p. 259°, and gives scarlet-red salts; the acetyl derivative forms violet crystals, m. p. 329° (decomp.).

2-*o*-Tolidino-α-naphthaquinone is a dark violet powder; the acetyl derivative,  $\text{C}_{26}\text{H}_{22}\text{O}_3\text{N}_2$ , crystallises in spindle-shaped prisms, m. p. 233°.

2-*o*,*o'*-Dichlorobenzidino-α-naphthaquinone,  $\text{C}_{22}\text{H}_{14}\text{O}_2\text{N}_2\text{Cl}_2$ , has m. p. 237° with previous sintering; the acetyl and benzoyl derivatives crystallise in plates having a coppery lustre, m. p. 264° and 302° respectively.

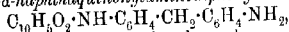
*N*,*p*-Aminophenyl-*N'*,*p*-2-α-naphthaquinonylamino, phenylcarbamide,  $\text{C}_{10}\text{H}_7\text{O}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , prepared from *p*:*p'*-diaminodiphenylcarbamide and α-naphthaquinone in glacial acetic acid solution, has m. p. 348°.

4-Amino-4'-(2)-α-naphthaquinonylamino, benzophenone,



prepared from 4:4'-diaminobenzophenone, crystallises in flat, brick-red prisms.

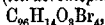
4-Amino-4'-(2)-α-naphthaquinonylamino, diphenylmethane,



prepared from 4:4'-diaminodiphenylmethane, has m. p. 182°. F. B.

**Preparation of 2:2'-Dianthraquinonylcarbamide.** FARBERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 232739).—The preparation of arylanthraquinonylcarbamides has previously been described (this vol., i, 469); it is now found that the action of carbonyl chloride at 170° on a nitrobenzene solution of 2-aminoanthraquinone forms initially 2-anthraquinonylcarbamide chloride, which then combines with another molecule of the base, yielding 2:2'-dianthraquinonylcarbamide, which separates in small, orange crystals. F. M. G. M.

**Condensation of Anthraquinone with Phenols.** WASSILI W. SCHARWIN [with K. A. KUSNEZOFF, W. A. NAYMOFF, A. L. GANDURIN, N. I. BERNKOFF, and S. A. DMITRIEFF] (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 562—574).—Most of this work has been already published (*Abstr.*, 1903, i, 640; 1904, i, 1032), the new matter being as follows.

*Tetrabromophenolanthrone (tetrabromophenolanthraquinone),*

forms colourless needles, m. p. 290°.

*Dinitrophenolanthrone*,  $\text{C}_{26}\text{H}_{10}\text{O}_2\text{N}_2$ , forms shining, yellow plates with a faint green tint, m. p. 236°; in alkaline solution it gives a pure, bright yellow coloration, which, as with other nitrophenols (compare Scharwin, Abstr., 1910, ii, 396), increases in intensity on dilution.

*Tetranitrophenolanthrone*,  $\text{C}_{26}\text{H}_{10}\text{O}_2\text{N}_4$ , forms lemon-yellow needles, m. p. 278°, and, in an acid-bath, dyes wool and silk bright yellow. *Hexanitrophenolanthrone*,  $\text{C}_{26}\text{H}_{10}\text{O}_2\text{N}_6$ , was also prepared.

*Dinitroresorcinolanthrone*,  $\text{C}_{26}\text{H}_{14}\text{O}_3\text{N}_2$ , and *tetramethoxydiphenylanthrone*,  $\text{CO} < \text{C}_6\text{H}_4 > \text{C}[\text{C}_6\text{H}_3(\text{OMe})_2]_2$ , were obtained as yellow powders; hydrolysis of the latter by means of aluminium chloride yields resorcinolanthrone.

T. H. P.

**Synthesis of Orthoquinones.** CARL LIEBERMANN (*Ber.*, 1911, 44, 1453—1455. Compare Liebermann and Zeuffa, this vol., i, 202, 387).—*p*-Ditolyl condenses with oxalyl chloride and aluminium chloride, yielding 2:7-dimethylphenanthraquinone together with 4:4'-dimethyldiphenic acid.

2:7-Dimethylphenanthraquinone,  $\text{C}_{18}\text{H}_{12}\text{O}_2$ , crystallises from alcohol in glistening, orange-red plates, m. p. 224°, and gives a green solution in concentrated sulphuric acid. The corresponding quinol is unstable,

but yields a stable *diacetyl* derivative,  $\text{C}_6\text{H}_3\text{Me}\cdot\text{CH}\cdot\text{OAc}$ , in the form of colourless, glistening plates, m. p. 202°.

4:4'-Dimethyldiphenic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}_2\text{H}$ , has m. p. 324°. The calcium salt crystallises in transparent prisms containing  $2\text{H}_2\text{O}$ .

J. J. S.

**Colloidal Chemical Observations on the Pyranthrone Vat Dyes.** ROLAND SCHOLL (*Ber.*, 1911, 44, 1448—1452).—Pyranthrone yields a purple-red vat dye when reduced with a hot alkaline solution of sodium hyposulphite (Abstr., 1910, i, 271) and a yellow cherry-red vat when reduced at the ordinary temperature. Both products react with *p*-bromobenzoyl chloride, yielding di-*p*-bromobenzoyltetrahydropyranthrone, which differ somewhat in appearance, but when the compound from the cherry-red vat is crystallised several times from nitrobenzene, it has the same appearance as the product from the purple-red vat. The conclusion drawn is that the cold vat consists essentially of the same tetrahydropyranthrone as the hot vat, and that its cherry-red colour is due to a small amount of impurity, namely, colloidal pyranthrone, which forms a colloidal complex with the vat.

Experiments are described which support this view.

The formation of lighter tones by immersing fabrics dyed with pyranthrone in boiling soap solution is shown to be due to a process of oxidation, and the same results can be obtained by exposing the dyed fabric to a 10% solution of sodium hydroxide containing a little potassium ferricyanide and to dilute alkali and atmospheric oxygen. The deeper tone can be restored by treatment with alkaline hypo-

sulphite solution, slowly at the ordinary temperature and more rapidly by warming.

Tetrahydropyranthrone can be obtained by allowing the vat, obtained by using hot alkaline hyposulphite, to cool in an atmosphere of hydrogen and then precipitating with dilute acetic acid. When dry, the precipitate has a yellowish-red colour, and gives a violet-red solution in sodium hydroxide.

When kept for some hours, the precipitate becomes darker, and yields an opalescent, brown solution with sodium hydroxide, probably containing dihydropyranthrone, as it turns yellow when shaken with air, owing to the formation of pyranthrone, and violet-red when treated with hyposulphite solution.

J. J. S.

**$\beta$ -Camphor (Bornylone) from Bornylenecarboxylic Acid.**  
JULIUS BREDT and W. HILBING (*Chem. Zeit.*, 1911, 35, 765).—An

account of the synthesis of  $\beta$ -camphor,  $\begin{array}{c} \text{CH}_2-\text{CH}-\text{CO} \\ | \quad | \\ \text{CH}_2-\text{CMe}-\text{CH}_2 \\ | \quad | \\ \text{CH}_2-\text{CMe}-\text{CH}_2 \end{array}$ , from

bornylenecarboxylic acid (Bredt, Abstr., 1906, i, 680; 1909, i, 499). *Bornylenecarboxyl chloride*,  $\text{C}_{10}\text{H}_{15}\cdot\text{COCl}$ , b. p. 114–115°/14 mm., when treated with hydrazine hydrate, yields the corresponding *hydrazide*,  $\text{C}_{10}\text{H}_{15}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ , m. p. 109–110°, which is converted, according to the method of Curtius, into the *azide*,  $\text{C}_{10}\text{H}_{15}\cdot\text{CO}\cdot\text{N}_3$ , and then into  *$\beta$ -iminocamphor*. On hydrolysis with acids, this yields  $\beta$ -camphor, b. p. 213.1–213.4°, m. p. 184–185°, which is identical with the *epicamphor* (of m. p. 185°) recently described by Lankshear and Perkin (*Proc.*, 1911, 27, 166).

On oxidation with nitric acid,  $\beta$ -camphor yields camphoric acid.

The oxime has m. p. 103–104°; the semicarbazone, m. p. 237° (compare Lankshear and Perkin, *loc. cit.*).

Wagner's (*Chem. Zeit.*, 1903, 27, 721)  $\beta$ -camphor consists mainly of ordinary camphor.

F. B.

**Hydrogenation of Limonene.** GUSTAVE VAYON (*Compt. rend.*, 1911, 152, 1675–1677).—Determination of the rate at which limonene absorbs hydrogen in presence of platinum-black shows that the hydrogenation takes place in two stages, enabling the dihydride or tetrahydride to be obtained at will. *Dihydrolimonene*,  $\text{C}_{10}\text{H}_{18}$ , has physical constants approaching those of  $\Delta^1$ -tetrahydro-*p*-cymene (carvomenthene): b. p. 175–177°,  $n_D^{20}$  1.4563,  $D_4^{20}$  0.8246,  $[\alpha]_{D^{20}}^{25} +118^\circ$ ,  $[\alpha]_{A^{436}}^{25} +234^\circ$ ; the *dibromide*,  $\text{C}_{10}\text{H}_{18}\text{Br}_2$ , has b. p. 136–140°/16 mm.,  $n_D^{20}$  1.5236,  $D_4^{20}$  1.459,  $[\alpha]_{A^{578}}^{25} +49^\circ$ ,  $[\alpha]_{A^{436}}^{25} +100^\circ$ . The *nitrosocchloride*,  $\text{C}_{10}\text{H}_{18}\text{ONCl}$ , remarkable for its high rotatory power, has m. p. 95–96°,  $[\alpha]_{A^{578}}^{25} +344^\circ$ ,  $[\alpha]_{A^{436}}^{25} +724^\circ$ ; the racemic form has been described by Wallach (this vol., i., 470).

W. O. W.

**Chemistry of Caoutchouc.** Theory of Vulcanisation. D. SPENCE and J. H. SCOTT (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 304–312).—The properties of vulcanised caoutchouc have been examined in relation to the chemical and the absorption theories of



vulcanisation. It is found that a portion of the sulphur cannot be removed either by the action of acetone or hot sodium hydroxide solution. When the vulcanised caoutchouc is treated with bromine by Budde's method, the product obtained contains sulphur and bromine in proportions which indicate that four atoms of bromine in the tetrabromide,  $C_{10}H_{16}Br_4$ , are in fact replaced by two atoms of sulphur. This equivalence of the "fixed" sulphur and the bromine is regarded as strong evidence in favour of the chemical combination of the "fixed" sulphur. Experiments, in which the quantities of sulphur removed by acetone in successive equal extraction periods were measured, indicate that a portion of the so-called "free" sulphur is adsorbed. The curves obtained by plotting the successive quantities of extracted sulphur against the period of extraction are in agreement with the requirements of an exponential adsorption equation.

From these results the following conclusions are drawn: (1) the "fixed" sulphur is chemically combined with the caoutchouc; (2) the "free" sulphur, that is to say, the portion which can be removed by solvents, is, in part, adsorbed, the remainder being present in the non-adsorbed condition. The amount of the non-adsorbed free sulphur is dependent on the conditions of the vulcanising process.

H. M. D.

**Essential Oil of Bupleurum fruticosum.** LUIGI FRANCESCONI and G. SANNA (*Gazzetta*, 1911, 41, i, 395—414).—The authors have examined the yield and properties of the essential oil obtained from specimens of *Bupleurum fruticosum* in different stages of development and from different localities.

The value of  $D^{15}$  varies from 0.8257 to 0.8692; the diminution per  $1^\circ$  rise of temperature is about 0.0008. The specific rotation varies for plants from different places and for the essences yielded by different organs; its maximum and minimum were found to be  $+45.5^\circ$  and  $+19.72^\circ$  respectively. The rotation diminishes with lapse of time, whilst the density increases. The value of  $n_D$  is 1.4783—1.4862, and the b. p. varies for any sample between about  $167^\circ$  and  $200^\circ$ .

In the air and light, it readily oxidises, forming a resinous substance, and this change may also be induced by heating in absence of air for three to four hours at  $210^\circ$ .

The yield of essential oil increases with the development of the plant, and during the periods of advanced and complete inflorescence is greater for the flowers than for the leaves. The density, rotation, and index of refraction increase up to the beginning of flowering and then diminish. The ester content is greater in plants growing at great altitudes, and diminishes with increase of the moisture in the air of the region. The rotatory power varies inversely, and the density directly, with the ester content. The amount of free alcohol is greater in the flowers than in the leaves, and increases in relation to the combined alcohol as flowering progresses. The principal constituents of the essential oil are hydrocarbons. T. H. P.

**Essential Oil of Wallflowers.** KUMMERT (*Chem. Zeit.*, 1911, 73, 667—668).—With low-boiling solvents, the blooms of *Cheiranthus Cheiri* yield a dark unctuous extract, which, when freed from fatty

matter by strong alcohol and distilled with steam, gives about 0.06% of a yellow, evil-smelling oil, showing in alcoholic solution a slightly blue fluorescence. Distilled under low pressure (3 mm.), less than 1% comes over at 40°, consisting mainly of tear-producing sulphur and nitrogen compounds, resembling mustard oil, which probably unite in the seed-pods to complex molecules, producing the substance cheirolin discovered by Schneider (Abstr., 1909, i, 826; 1910, i, 658). The higher fractions contain aldehydes and ketones, which were separated by their carbazones. These, on treatment with oxalic acid, gave a distinct odour of violets (irone?) and hawthorn (anisaldehyde?). The oil, freed from aldehydes and ketones, was saponified with alcoholic potash, washed, steam-distilled, dried in vacuum, and heated in the water-bath with benzene and phthalic anhydride. The primary alcohols nerol, geraniol, and benzyl alcohol were identified. In the neutral oil, linalool was detected. From the potassium hydroxide extract were obtained phenols (*p*-cresol?) and lactones (coumarin-like substances), acetic, salicylic and anthranilic acids.

The last small fractions contained methyl anthranilate and indole, along with substances smelling like pyridine.

J. D. K.

**Meliatin, a New Glucoside Hydrolysable by Emulsin**, obtained from the Marsh Trefoil. MARC BRIDEL (*Compt. rend.*, 1911, 152, 1694—1696).—A new glucoside, *meliatin*,  $C_{16}H_{26}O_{10}$ , has been extracted from the marsh trefoil (*Menyanthes trifoliata*) by extraction with alcohol. The compound occurs in colourless crystals with a bitter taste, m. p. 222° (corr.),  $[\alpha]_D - 81.96^\circ$  in aqueous solution. It undergoes hydrolysis by emulsin with production of dextrose.

W. O. W.

**Preparation of Mixed Formic Acetic Esters of Aloins.** FÄRDEFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 233326).—When aloin is heated at 100° with a mixture of formic and acetic acids (or with formic acetic anhydride) in the presence of zinc chloride, mixed esters are produced.

The ester, containing two formyl and three acetyl residues, forms an almost tasteless, yellow powder, decomposing at 75—90°.

F. M. G. M.

**Chlorophyll. XVI. The Primary Decompositions of Chlorophyll.** RICHARD WILLSTÄTTER and MAX UTZINGER (*Annalen*, 1911, 382, 129—194).—Crystalline chlorophyll (ethylchlorophyllide) (Willstätter and Benz, Abstr., 1908, i, 199; Willstätter and Stoll, this vol., i, 142) consists of two definite compounds, *a* and *b* (compare Willstätter and Isler, this vol., i, 392). The analysis of the product dried over phosphoric oxide in the vacuum of a water-pump agrees with the formula  $C_{55}H_{84}O_7N_4Mg$ , not  $C_{55}H_{82}O_7N_4Mg$ ; when heated at 100—105°/0.001—0.01 mm., a further loss of about 5% occurs, probably due to water and ether, and the residue has a composition corresponding with the formula  $C_{57}H_{88}O_5N_4Mg$ . It is suggested that this probably consists of a mixture of the chlorophyllide-*a*,  $C_{57}H_{88}O_5N_4Mg$ , and chlorophyllide-*b*,  $C_{55}H_{84}O_7N_4Mg$  (or  $C_{57}H_{88}O_5N_4Mg$ ), in the ratio 2.5:1. The *a* compound is regarded as a mixture of practically

equal parts of the lactam,  $C_{87}H_{88}O_5N_4Mg$ , and the lactam hydrate,  $C_{87}H_{90}O_6N_4Mg$ .

The ethylchlorophyllide, dried at  $100-105^\circ$ , yields methyl and ethyl iodides in molecular proportions when heated with hydriodic acid. It is shown that these two alkyl iodides can be recognised and separated by conversion into quaternary ammonium salts. This can be accomplished by the aid of dimethylaniline in the absence of alcohol, or by means of an alcoholic solution of trimethylamine. Dimethylaniline reacts with methyl iodide much more readily than with ethyl iodide; for example, after six hours 95% of the methyl iodide has combined, whereas only 8% of the ethyl iodide has reacted. The separation can also be accomplished by means of the different solubilities of the two quaternary ammonium iodides. Phenyltrimethylammonium iodide is very sparingly soluble in chloroform, whereas phenyldimethylethylammonium iodide, m. p.  $136^\circ$ , dissolves with the greatest readiness. With trimethylamine the separation is even more marked, especially with absolute alcohol as solvent. One gram of tetramethylammonium iodide dissolves in 1060 grams of absolute alcohol, whereas 1 gram of trimethylethylammonium iodide dissolves in 1.23 grams of absolute alcohol.

A slightly modified method for the isolation of ethylchlorophyllide is described; it consists in removing the colouring matter from its alcoholic solution by ether, drying with sodium sulphate, evaporating until the solution has a thick consistency, then mixing well with talc, keeping for a day, then filtering, and washing well with ether. The mixture of talc and coloured crystals, which is free from yellow pigments, is then extracted with alcohol (not absolute), mixed rapidly with ether, and the alcohol removed by washing. The ethereal solution when evaporated slowly yields crystals of ethylchlorophyllide. Two points of importance in the isolation are: (a) sufficient time must be allowed for the complete ethanolysis of the original chlorophyll to ethylchlorophyllide (Willstätter and Stoll, this vol., i, 141); (b) the alcohol must contain water; previously 96% alcohol was recommended, but 10% of water increases the rate of alcoholysis.

Different specimens of ethylchlorophyllide differ somewhat in appearance; in solution under the microscope some are bluish-green and others yellowish-green. These differences are probably due to the different amounts of the *a* and *b* compounds present. Some preparations are sparingly soluble in ether (1 gram in 2.5 litres), but the products dried at  $100^\circ$  under reduced pressure are extremely readily soluble in absolute ether, although when hydrolysed by alkali they give the characteristic brown phase.

Ethylchlorophyllide undergoes a change when kept for some time in absolute ethyl or methyl alcohol, and the products formed no longer give the brown phase when hydrolysed by alkalis. The altered compound dissolves readily in ether, cannot be crystallised, but is thrown down as a bluish-black powder on the addition of light petroleum to its ethereal solution. When fractionally precipitated, the first fraction is more yellowish-green and the last distinctly blue. Analyses of the product formed by the action of methyl

alcohol agree with the view that half a molecule of water and half a molecule of methyl alcohol have combined with the ethylchlorophyllide.

Ethylphæophorbide, the product free from magnesium formed by the action of cold acids on ethylchlorophyllide, consists of two distinct compounds.\* It is obtained crystalline by the action of a saturated ethereal solution of hydrated oxalic acid on an ethereal solution of the chlorophyllide. At the end of two days, large brownish-black plates with a metallic lustre are deposited (Fraction I), and from the mother liquors, after removal of oxalic acid, long, pointed prisms are obtained (Fraction II). Both fractions can be recrystallised by solution in chloroform, mixing with a little ether, and pouring into much ether; fraction II can also be crystallised from ether. Fraction I is extremely sparingly soluble in cold alcohol or ether; its solutions in most organic solvents have a reddish-olive colour, but its solution in formic acid is bluish-green. When hydrolysed with alcoholic potash, it yields much phytorhodin-*g*, together with phytochlorin-*e*. Fraction II is more readily soluble in ether; its solutions are generally olive-green, but that in formic acid is blue. When hydrolysed with alkalis, it yields mainly phytochlorin-*e*, together with a very small amount of phytorhodin. Molecular-weight determinations of ethylchlorophyllide, ethylphæophorbide, and other products by cryoscopic and ebullioscopic methods indicate that they have not the double formulæ.

When chlorophyll-*a* in light petroleum solution is hydrolysed with 7% methyl-alcoholic potassium hydroxide, the potassium salt of chlorophyllin,  $C_{54}H_{84}O_6N_4MgK_2$  (compare Willstätter and Fritzsche, *Abstr.*, 1910, i, 126), separates as glistening, dark blue plates, which appear pure green under the microscope in transmitted light. The salt is not quite pure, and contains about 1% of methoxyl.

When decomposed with hydrochloric acid, it yields phytochlorin-*g*, which can be extracted from its ethereal solution by 1% hydrochloric acid.

When the chlorophyllin salt is heated in sealed vessels with alcoholic potassium hydroxide, it yields glaucophyllin, then rhodophyllin, and finally pyrrophyllin (Willstätter and Fritzsche, *loc. cit.*). A different chlorophyllin, *isochlorophyllin*, is formed when chlorophyll-*a* in pyridine solution is hydrolysed with warm alcoholic potassium hydroxide. The potassium salt could not be isolated in the form of good crystals, and contained too little nitrogen and magnesium. The calcium salt forms a pale green, flocculent precipitate. When decomposed with hydrochloric acid, the *isochlorophyllin* yields phytochlorin-*e*, and when heated with alcoholic potassium hydroxide at 150°, it yields a phyllin the alkaline and ethereal solutions of which are deep blue. With alcoholic potassium hydroxide at 225–230°, it yields a phyllin identical with or closely allied to phyllophyllin. The ammonium and calcium salts are soluble in ether, and the calcium salt sparingly soluble in chloroform.

Phytochlorin-*e* can be obtained by hydrolysing crude chlorophyll extract with barium hydroxide, dissolving the barium salt of *isochlorophyllin* in ether, and shaking with 16% hydrochloric acid.

Alcoholic potassium hydroxide can react with phaeophytin and ethylphosphoribide in two different ways, according to the conditions of the experiment.

With concentrated alcoholic potassium hydroxide, either cold or hot, the products are phytochlorin-*e* and phytorhodin-*g*. By the action of alcoholic potash on an ethereal solution of alkylphosphoribides, phytochlorin-*g* is formed together with a faintly basic phytorhodin—phytorhodin-*i* or a similar compound. These two processes correspond with the hydrolysis of chlorophyll by hot and by cold potassium hydroxide solution.

The analyses of various specimens of phytochlorin-*e* do not agree, and this is shown to be due to the fact that the compounds exist in two forms, which differ in the amount of water they contain, namely,  $C_{54}H_{53}O_6N_4$  and  $C_{54}H_{50}O_6N_4$ , termed respectively the *lactam* and *lactam-hydrate*. It is possible that the two can unite to form a definite compound, which would be a half hydrate like many other chlorophyll derivatives.

In the isolation of the hydrate, it is essential that the method of extraction and purification should not entail prolonged treatment with hydrochloric acid, as this converts the hydrate into the lactam. The hydrate forms compact, opaque, crystalline plates with a violet lustre; the lactam, small, glistening plates which appear black to the eye. They are doubly refractive, and the colours in transmitted light are pale green, olive-green, and brown. Both compounds lose in weight when heated at  $105^{\circ}/0.01$  mm. The lactam loses some 3%, and the hydrate 0.5 to 1%. The hydrate is quite stable, and is unaltered at the end of nine months. The lactam crystals are also stable, but after drying in a desiccator they undergo decomposition when kept; at the end of nine months an appreciable amount of a rhodum, probably phytorhodin-*h*, is present, together with phytochlorin-*f*. The lactam dissolves more readily than the hydrate in most solvents. The hydrate is extremely sparingly soluble in cold alcohol, and is insoluble in chloroform. Its solution in formic acid is blue and in pyridine olive-coloured. Concentrated hydrochloric acid does not decompose phytochlorin-*e*, but concentrated sulphuric acid transforms it into an amorphous product insoluble in ether. With acetic anhydride, the phytochlorin yields glistening, bluish-black, rhombic plates, and when oxidised with chromium trioxide in sulphuric acid solution, it yields a mixture of acid and neutral products, including methylethylmaleinimide and the imide of hematic acid. When heated with crystallised phosphoric acid at  $140^{\circ}$ , it yields phylloporphyrin, but at  $100^{\circ}$  it yields only a small amount of phylloporphyrin, together with phytochlorin-*h*, which dissolves in dilute hydrochloric acid, giving a reddish-violet solution. It is formed from the original phytochlorin by the elimination of carbon dioxide. The following salts of phytochlorin-*e* have been prepared:  $C_{54}H_{53}O_6N_4K_2$ , brown, rectangular plates;  $C_{54}H_{53}O_6N_4C_8H_8$  and  $C_{54}H_{50}O_6N_4NH_4$ . The trimethyl ester,  $C_{54}H_{53}N_4(CO_2Me)_3$ , obtained from the potassium salt and methyl sulphate, separated in steel-blue, felted prisms, m. p.  $188-190^{\circ}$ . The compound is also partly esterified by methyl alcohol and hydrogen chloride.

Phytochlorin-*f* (Willstätter and Isler, this vol., i, 392; Willstätter and Hocheder, Abstr., 1907, i, 785) has not been obtained from chlorophyllin-*a*. It has the formula  $C_{34}H_{34}O_8N_4$ , and loses but little in weight when dried at  $105^\circ$  under reduced pressure, and is sparingly soluble in most solvents, with the exception of formic acid and pyridine. The solution of the ammonium salt in ether has a brilliant green colour, and the solution in hydrochloric acid (10%) has a pure blue colour. The *caesium* salt,  $C_{34}H_{31}O_8N_4Cs_2$ , forms glistening, steel-blue prisms; the *methyl* ester,  $C_{36}H_{36}O_8N_4(1)$ , forms blue, monoclinic, six-sided plates or prisms, and is less basic than the acid.

Phytochlorin-*g* is formed also when chlorophyll-*a* is kept for some time in light petroleum, and then hydrolysed with alcoholic potassium hydroxide and acidified. Its ethereal solution is olive-green, but turns brown when kept. The hydrochloric acid number is 10–11, and the solution in acid is bluish-green. When evaporated and warmed for a short time with alcohol, an unstable, brilliant red product is formed. When heated with alcoholic potassium hydroxide in silver vessels at  $140$ – $150^\circ$ , phytochlorin-*g* yields a dicarboxylic product similar to glaucoporphyrin (Willstätter and Fritzsche, Abstr., 1910, i, 127); its hydrochloride is, however, less soluble, and the colours of its solutions are somewhat different. With alcoholic potassium hydroxide at  $225$ – $230^\circ$ , phytochlorin-*g* yields pyrroporphyrin. Phytochlorin-*f*, when heated for seven hours at  $140$ – $150^\circ$  with alcoholic potassium hydroxide, yields rhodoporphyrin, and at  $200^\circ$  yields pyrroporphyrin. Phytochlorin-*e* and alcoholic potassium hydroxide at  $140$ – $150^\circ$  yield the monocarboxylic phylloporphyrin, the *methyl* ester of which,  $C_{33}H_{38}O_8N_4$ , crystallises from ether or acetone, has m. p.  $224^\circ$  after sintering at  $220^\circ$ , and acid number 1–1.25.

Phytorhodin-*g*,  $C_{34}H_{34}O_7N_4$ , is formed from the *b*-chlorophyll component of all plants by hydrolysing the phæophytin or phæophorbide in undiluted form with alkali. It is also formed from isochlorophyllin and acid, and crystallises in compact, glistening, black, six-sided prisms, and appears to be a tribasic acid. A hydrated form also exists,  $C_{34}H_{36}O_8N_4$ . It is a strongly acid compound, and is removed from its ethereal solution by 0.001% ammonia. Its solution in dilute alcoholic potassium hydroxide has a deep red colour, but in concentrated, a green colour. The *potassium* salt,

$C_{34}H_{31}O_7N_4K_3$ , blackish-brown plates, *caesium* salt,  $C_{34}H_{29}O_7N_4Cs_3$ , rhombic plates, and *methyl* ester,  $C_{37}H_{40}O_7N_4$ , glistening, black, rectangular plates and prisms, m. p.  $207$ – $210^\circ$ , have been prepared.

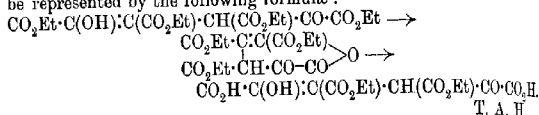
Phytorhodin-*i*,  $C_{34}H_{32}O_8N_4$ , the feebly basic phytorhodin previously described (this vol., i, 392), crystallises in brown or black, microscopic plates; its ethereal solution is brownish-red, and its solution in hydrochloric acid green. Its *potassium* salt is sparingly soluble in water. With alcoholic potassium hydroxide at  $150^\circ$ , it yields a dibasic porphyrin similar to rhodoporphyrin, and at  $200^\circ$  the monobasic pyrroporphyrin.

The relationships of many of the compounds are discussed.

J. J. S.

**Dibasic Ketonic Acids. III.** EDMOND E. BLAISE and HENRI GAULT (*Bull. Soc. chim.*, 1911, [iv], 9, 588—592).—This paper gives in greater detail, with some modifications, the results described already (Abstr., 1908, i, 713; 1909, i, 134).

Ethyl dioxalylsuccinate on hydrolysis by hydrochloric acid in the cold furnishes 3-hydroxy-2-pyrone-6-carboxylic acid, m. p. 87° (approx.), which crystallises in colourless needles, gives a violet coloration with ferric chloride, a green coloration with pine wood moistened with hydrochloric acid, and reduces ammoniacal silver nitrate slowly in the cold and immediately on warming. When heated at 150°, it furnishes isopyromucic acid (3-hydroxy-2-pyrone), m. p. 87°, by loss of carbon dioxide (*loc. cit.*, Chavanne, Abstr., 1904, i, 82). In view of these results the authors suggest that the lactone and its derivatives obtained by Wislicenus and Boeckler (Abstr., 1895, i, 506) by the action of alkalis on ethyl dioxalylsuccinate should be represented by the following formulae:



**Migration of Phenyl in the Synthesis of Phenylated Coumarones.** Phosphorus Tribromide as a Reducing Agent. III. RICHARD STOEHRER (*Ber.*, 1911, 44, 1853—1865. Compare Abstr., 1904, i, 181; 1907, i, 446).—Aromatic  $\gamma$ -lactones, such as the lactone of phenyl-*p*-hydroxytolylacetic acid, when heated with phosphorus tribromide under ordinary pressure at a high temperature form 2-phenylated coumarones, whereas above 200° under pressure 1-phenylated compounds are also formed. It is supposed that an intermediate unsaturated compound is formed and not a brominated phenylcoumarone, which, when prepared in another manner, is not altered on heating with phosphorus tribromide. Similarly, 2-phenylcoumarone is unaltered by heating with phosphorus tribromide.

The lactone of dibromohydroxydiphenylacetic acid could not be converted into bromophenylcoumarone in this manner.

The tendency of the phenyl group to wander to position (1) is but small, and it is destroyed by the introduction of substituents.

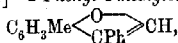
The synthesis of 1-phenylcoumarone has been effected from homosalicylaldehyde and chlorophenylacetic acid in order to establish its constitution. Characteristic of this is the yellow coloration with concentrated sulphuric acid, which soon turns green.

1-Bromo-2-phenylcoumarone interacts very readily with nitrous fumes, forming 1-nitro-2-phenylcoumarone. This is still more conveniently prepared by dissolving the brominated coumarone in acetic acid, adding a little nitric acid and sodium nitrite, and warming until the bromine vapour has all been given off. On pouring into water, the nitro-compound is now obtained pure. Presumably an additive product with nitrogen trioxide is first formed, from which nitrosyl bromide is subsequently eliminated.

With phosphoryl chloride under pressure, 1-chloro-2-phenyl

coumarone is obtained, and no migration of phenyl takes place. This product cannot be reduced to the chlorine-free compound.

[With CLAUD DECKER.]—2-Phenyl-4-methylcoumarone,



has b. p.  $193^\circ/20$  mm., does not solidify on cooling, and gives an intense red coloration with concentrated sulphuric acid. It forms 2-phenyl-4-methylcoumarone on reduction.

1-Phenyl-4-methylcoumarone,  $\text{CH}_3 \cdot \text{C}_6\text{H}_3 \begin{array}{c} \diagup \text{O} \diagdown \\ \text{CH} \end{array} \text{CPh}$ , forms colourless, matted needles, m. p.  $129^\circ$ .

1-Bromo-2-phenyl-4-methylcoumarone crystallises in stellar aggregates of needles, m. p.  $65^\circ$ , which show a faint red coloration with concentrated sulphuric acid.

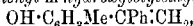
1-Nitro-2-phenyl-4-methylcoumarone forms radially-grouped, yellow needles, m. p.  $115-116^\circ$ .

1-Bromo-2-phenylcoumarone is an oil of sweet odour, b. p.  $195^\circ/20$  mm. 1-Nitro-2-phenylcoumarone separates in long, yellow needles, m. p.  $105^\circ$ . The bromo-derivative of 1-phenylcoumarone has b. p.  $203^\circ/23$  mm., crystallising in lustrous, silvery platelets, m. p.  $81^\circ$ . Nitrous acid is without action on it.

The lactone of phenyl-*m*-hydroxytolylacetic acid (annexed formula) when heated with phosphoryl chloride at  $130^\circ$  forms 1-chloro-2-phenyl-5-methylcoumarone, b. p.  $175^\circ/10$  mm., crystallising in needles of silvery lustre, m. p.  $85.5^\circ$ . On reduction of this chloride, or of the corresponding bromide,

2-phenyl-5-methylcoumarone is obtained in small, colourless needles, m. p.  $45^\circ$ , b. p.  $170^\circ/14$  mm. This, when brominated in acetic acid, is converted into 4(?)-bromo-5-methyl-2-phenylcoumarone, which crystallises in short, pointed needles, m. p.  $125^\circ$ .

Phenylmethylcoumarone when heated with alkali hydroxide at  $200^\circ$  under pressure yields phenyl-*m*-hydroxytolylethylene,



a colourless oil, b. p.  $205^\circ/20$  mm., soluble in alkali, and becoming intense red with concentrated sulphuric acid.

2-Phenyl-5-methylcoumarone, obtained by the action of phosphorus tribromide on the lactone of phenyl-*m*-hydroxytolylacetic acid, forms short needles, m. p.  $31^\circ$ , b. p.  $168^\circ/18$  mm., and gives an intense orange coloration with concentrated sulphuric acid.

The isomeric 1-phenyl-5-methylcoumarone, obtained on more strongly heating, crystallises in silvery needles, m. p.  $135.5^\circ$ , and gives a yellow coloration with sulphuric acid, changing to dark green. This compound is identical with that obtained on condensing phenylchloroacetic acid with *m*-homosalicylaldehyde. Accordingly, the formula of the lactone of phenyl-*m*-hydroxytolylacetic acid is established as that given above.

1-Bromo-2-phenyl-5-methylcoumarone has m. p.  $95^\circ$ ; the corresponding 1-nitro-derivative forms small, yellow crystals, m. p.  $119-120^\circ$ .

The lactone of *o*-hydroxyphenylanisylacetic acid, prepared from anisaldehyde cyanohydrin, phenol, and sulphuric acid, forms colourless



needles, m. p. 178°. The corresponding anisylcoumarone could not be obtained.

*p*-Hydroxytolylanisylacetic acid lactone forms colourless plates, m. p. 135°. On heating with phosphorus tribromide, 2-anisyl-4-methylcoumarone is obtained in matted needles, m. p. 73.5°; this shows a strong eosin coloration with strong sulphuric acid.

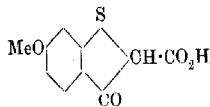
[With KARL HILDEBRANDT.]—The lactone of *p*-chloro-*o*-hydroxydiphenylacetic acid forms colourless needles, m. p. 125°; the corresponding bromo-compound is very similar, m. p. 123°. On heating with phosphoryl chloride, 1-chloro-2-*p*-chlorophenylcoumarone is obtained in long, silvery needles, m. p. 122°.

2-*p*-Chlorophenylcoumarone, m. p. 34°, gives an orange coloration with sulphuric acid; the isomeric 1-phenyl derivative could not be obtained.

1-Chloro-2-*p*-bromophenylcoumarone forms long, lustrous needles, m. p. 119°.

2-*p*-Bromophenylcoumarone crystallises in long, matted needles, m. p. 38°, giving an orange-red coloration with sulphuric acid. The 1-phenyl compound could not be detected. E. F. A.

Preparation of Alkyloxy- and Alkylthio-derivatives of 3-Hydroxy-(1)-thionaphthen-2-carboxylic Acid. KALLE & Co. (D.R.-P. 232377. Compare Abstr., 1908, i, 451, 797).—The preparation of 3-hydroxy-(1)-thionaphthen-2-carboxylic acid from phenyl-*o*-carboxymethylthiolbenzoic acid has been recorded previously, and the preparation of its alkyloxy- and alkylthio-derivatives containing the substituted group in the benzene ring is now described.



3-Keto-6-methoxy-(1)-thionaphthen-2-carboxylic acid (annexed formula), yielding a yellow nitroso-derivative and converted by boiling dilute hydrochloric acid into

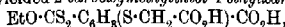
3-keto-6-methoxy-(1)-thionaphthen (needles, m. p. 118—119°), was prepared by the following series of operations.

*o*-Amino-*p*-cresol was acetylated, and subsequently methylated with methyl sulphate in alkaline solution, yielding *o*-acetylaminio-*p*-tolyl methyl ether, needles, m. p. 96°; this was oxidised to 2-acetylaminio-4-methoxybenzoic acid, colourless needles, m. p. 197—199°, which by successive hydrolysis, diazotisation, xanthogenation, and treatment with chloroacetic acid, yielded 6-methoxyphenylthioglycol-*o*-carboxylic acid, needles, m. p. 224—225°; this acid when fused at 180—200° with sodium hydroxide yielded the foregoing 6-methoxy-3-oxy-(1)-thionaphthen-2-carboxylic acid.

4-Acetylaminophenol-3-carboxylic acid, m. p. 224—226°, by similar treatment yielded 2-carboxymethylthiol-5-methoxybenzoic acid, yellow prisms, m. p. 197—199°, which was subsequently converted by fusion with alkali into 3-keto-5-methoxy-(1)-thionaphthen-2-carboxylic acid; this acid forms a nitroso-derivative (yellow needles, m. p. 208—209°), and is converted by boiling dilute hydrochloric acid into 3-keto-5-methoxy-(1)-thionaphthen, yellow needles, m. p. 102—104°.

3-Keto-6-ethylthiol-(1)-thionaphthen, yellow needles, m. p. 84—86°.

yielded a *nitroso-derivative*, and the following intermediate compounds were obtained in its preparation. 4-Acetylaminocanthranilic acid, m. p. 193—194°. 2-Carboxymethylthiol-4-acetylaminobenzoic acid, colourless needles, m. p. 249° (decomp.), which on hydrolysis, diazotisation, and xanthogenation yielded 2-carboxymethylthiol-4-ethylcanthobenzoic acid,



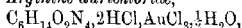
a yellowish-red powder, which was converted into 2-carboxymethylthiol-4-ethylthiolbenzoic acid, yellow needles, m. p. 188°. 3-Keto-6-ethyl-

thiol-(1)-thionaphthen-2-carboxylic acid,  $\text{SEt} \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{CH} \cdot \text{CO}_2\text{H}$ , a colourless powder, yielded a *nitroso-derivative*, glistening, reddish-yellow needles, m. p. 176°.

3-Keto-5-methylthiol-(1)-thionaphthen, yellow needles, m. p. 81—82°, yielded a *nitroso-derivative*, m. p. 178°, and was prepared through the following compounds: 2-carboxymethylthiol-5-acetylaminobenzoic acid (obtained from 5-acetylaminocanthranilic acid), colourless needles, m. p. 249—250°; 2-carboxymethylthiol-5-ethylcanthobenzoic acid, yellow crystals; 2-carboxymethylthiol-5-methylthiolbenzoic acid, yellow needles, m. p. 195°; and 3-keto-5-methylthiol-(1)-thionaphthen-2-carboxylic acid, which has no characteristic melting point. F. M. G. M.

[Preparation of Thionaphthen Derivatives.] KALLE & Co. (D.R.P. 232995).—Bistolythioglycollic acid, glistening leaflets, m. p. 167—168°, prepared by methods previously described (Abstr., 1880, 476), is converted by treatment with chlorosulphonic acid into *biketolythionaphthen*, and *biketophenylthionaphthen* is obtained in a similar manner from bisphenylthioglycollic acid. These oxythionaphthen derivatives furnish blue dyes on oxidation, and condense with compounds containing the groups CO-, CS-, C:NR, C:N·NHR, and CX<sub>2</sub> (where R is alkyl and X a halogen). F. M. G. M.

**Salts of Arginine.** FRITZ WEISS (Zeitsch. physiol. Chem., 1911, 72, 490—493).—*dl-Arginine aurichloride*,



separates from water in brownish-red, nodular masses, m. p. 105—115°. *d-Arginine aurichloride*,  $\text{C}_6\text{H}_{14}\text{O}_2\text{N}_4 \cdot 2\text{HAuCl}_{3/2} \cdot \frac{1}{2}\text{H}_2\text{O}$ , is somewhat more soluble in water than the *dl*-salt; it sinters at 140°, and has m. p. 160°. The *acid sulphate*,  $\text{C}_6\text{H}_{14}\text{O}_2\text{N}_4 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , forms hard, crystalline crusts from dilute alcohol with no definite m. p. The corresponding *d*-salt forms a deliquescent, crystalline powder.

J. J. S.

**Nitroclupeine.** ALBRECHT KOSSEL and E. L. KENNAWAY (Zeitsch. physiol. Chem., 1911, 72, 486—489).—By the addition of well cooled fuming nitric acid (1 c.c.) to a well stirred mixture of clupeine sulphate (2 grams), concentrated sulphuric acid (4 c.c.), and fuming sulphuric acid (2 c.c. of 10% SO<sub>3</sub>) cooled to 0°, and, after five to ten minutes, pouring the mass on to ice, it has been found possible to obtain a *nitroclupeine*, which dissolves in dilute sodium hydroxide solution and can be precipitated by the addition of dilute acid.

When hydrolysed with 30% sulphuric acid, the nitro-compound

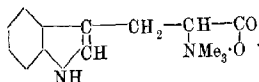
yields *nitroarginine*,  $C_6H_{13}O_4N_3$ , which crystallises from water, has m. p. 227—228°, and is dextrorotatory. It dissolves in dilute hydrochloric or nitric acid, and also in dilute ammonia.

A similar compound can be obtained by the action of nitric acid on *d*-arginine nitrate.  
J. J. S.

**Hypaphorine and the Relation of this Substance to Tryptophan.** PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 13, 1177—1180).—The alkaloid hypaphorine, found by Greshoff (*Abstr.*, 1891, i, 335) in the seeds of *Erythrina Hypaphorus* (the "dadap minjak" of Eastern Java), crystallises as a hydrate, efflorescing in a desiccator, m. p. 255°,  $[\alpha]_D +91-93^\circ$ . It yields a sparingly soluble nitrate.

Analysis of the anhydrous base agrees with the formula  $C_{17}H_{19}O_2N_3$ . When heated with strong aqueous potassium hydroxide, trimethylamine and indole are produced.

Tryptophan, treated with methyl iodide and sodium hydroxide in methyl alcohol, yields a substance, the nitrate of which closely resembles that



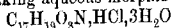
of hypaphorine, and gives on heating with aqueous potassium hydroxide the odour of amine and indole. It is considered that hypaphorine is most probably  $\alpha$ -trimethyl- $\beta$ -indolepropionetaine

(annexed formula) (Ellinger, *Abstr.*, 1907, i, 737). The investigation is being continued in conjunction with Barger, who has quite recently methylated tryptophan by the method of Engeland (*Abstr.*, 1910, i, 843), with like results.  
J. D. K.

**Preparation of Formyl Derivatives of Morphine Alkaloids.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.P. 233325).—The preparation of formyl derivatives of morphine alkaloids has been described previously (*Abstr.*, 1910, i, 765); it is now found that the reaction proceeds quantitatively and at the ordinary temperature if the anhydride of another paraffinoid acid (such as acetic) is employed in conjunction with the formic acid. Details of the preparation of formylcodeine and of formyl- $\beta$ -methylmorphimethine are given.

F. M. G. M.

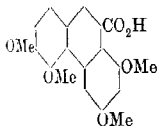
**Dihydromorphine.** J. OLDENBERG (*Ber.*, 1911, 44, 1829—1831).—Hitherto hydrogenised derivatives of morphine and codeine have not been obtained. By shaking aqueous morphine hydrochloride,



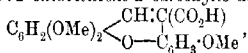
(10 grams in 250 c.c. of water), with aqueous colloidal palladium (0.1 gram in 10 c.c.) saturated with hydrogen, the author has obtained *dihydromorphine*,  $C_{17}H_{21}O_2N, H_2O$ , in colourless needles, m. p. 155—157°. The base has the same bitter after-taste and physiological action as morphine, reacts with ferric chloride in a similar manner, and instantly reduces silver nitrate; the *hydrochloride* and the *sulphate* are described.  
C. S.

**Constitution of Morphothebaine. II. Synthesis of the Tetramethoxyphenanthrene Derived from Morphothebaine.** ROBERT PSCHORR and GEORG KNÖFFLER (*Analen*, 1911, 382, 50—61. Compare Freund and Holthof, *Abstr.*, 1899, i, 308; Pschorr, *Abstr.*, 1904, i, 767; Knorr and Pschorr, 1905, i, 814).—The structural formula previously suggested (*Abstr.*, 1910, i, 423) for morphothebaine has been confirmed by synthesising 3:4:6:8-tetramethoxyphenanthrene and proving that it is identical with the product formed from morphothebaine.

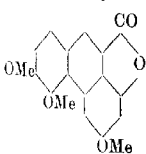
3:4-Dimethoxybenzaldehyde, hippuric acid, anhydrous sodium acetate, and acetic anhydride yield the *anhydride of benzoylamino-dimethoxycinnamic acid*,  $C_{18}H_{15}O_4N$ , which crystallises from dilute alcohol in colourless needles, m. p. 182° (corr.), and on hydrolysis with 10% sodium hydroxide solution yields dimethoxyphenylpyruvic acid and benzoic acid. The mixture of the two acids is oxidised with hydrogen peroxide in alkaline solution and then acidified and extracted with ether, when 50% of the 2:4-dimethoxyphenylacetic acid crystallises out on cooling to 0°. The remainder can be separated from benzoic acid by fractionation of the mixture of their ethyl esters. The acid,  $C_6H_3(OMe)_2 \cdot CH_2 \cdot CO_2H$ , crystallises in colourless needles, m. p. 113° (corr.), and its anhydrous sodium salt condenses with o-nitrovanillin methyl ether in the presence of acetic anhydride at 105—110°, yielding  $\alpha$ -2':4'-dimethoxyphenyl-2-nitro-3:4-dimethoxycinnamic acid,  $NO_2 \cdot C_6H_3(OMe)_2 \cdot CH : C(CO_2H) \cdot C_6H_3(OMe)_2$ . The acid is purified by means of its sparingly soluble ammonium salt, and crystallises in yellow plates, m. p. 232° (corr.). When reduced with ferrous sulphate in the presence of ammonium hydroxide, the nitro-acid yields the corresponding *amino-acid*,  $C_{19}H_{17}O_6N$ , which crystallises from methyl alcohol in yellow cubes, m. p. 207—208°. When dissolved in methyl alcohol and dilute sulphuric acid, diazotised by the addition of *N*-sodium nitrite solution, and the resulting solution heated on the water-bath, a 30% yield of 3:4:6:8-tetramethoxyphenanthrene-9-carboxylic acid (annexed formula) is obtained. It crystallises from methyl alcohol in plates, m. p. 226° (corr.).



By-products formed at the same time are:



well-developed prisms, m. p. 253°, and a product insoluble in ammonia. The tetramethoxy-acid when heated with glacial acetic acid at 240° for twenty hours yields 3:4:6:8-tetramethoxyphenanthrene (10% yield),



together with the *lactone* of 3:4:6-trimethoxy-8-hydroxyphenanthrene-9-carboxylic acid (annexed formula), m. p. 202—203°. On hydrolysis the lactone yields the corresponding acid, which crystallises from methyl alcohol in yellow prisms, m. p. 195°. With methyl sulphate, the acid yields *methyl* 3:4:6:8-tetramethoxyphenanthrene-9-carboxylate, m. p. 136—137°, which on hydrolysis gives the corresponding acid.

J. J. S.

**Preparation of Compounds from the Interaction of Cotarnine on Amides, Imides, or Ureides.** KNOLL & Co. (D.R.P. 232785).—The combination of cotarnine with amides, imides, or ureides yields a new class of compounds having therapeutic value.

Two *cotarnine- $\alpha$ -bromoisovalerylcaramides* have been prepared; one is obtained by mixing molecular proportions of cotarnine and  $\alpha$ -bromoisovalerylcaramide in alcoholic solution and allowing the mixture to remain until the product separates; it forms flat prisms, m. p. 125—127°, and is decomposed by dilute mineral acids into its generators. The second compound has m. p. 105—110°, and is prepared by employing two molecules of  $\alpha$ -bromoisovalerylcaramide in aqueous solution. The preparation of the following molecular compounds of cotarnine is also recorded: *cotarnineacetamide*, m. p. 135° (about); *cotarninecarbamide*, m. p. 180°; *cotarnineurethane*, m. p. 110°; and *cotarninephthalimide*, m. p. 130°.

F. M. G. M.

**Solanine Extracted from *Solanum sodomaeum*.** IV. GIUSEPPE ODDO and MARCELLO CESARIS (*Gazzetta*, 1911, 41, i, 490—534. Compare Abstr., 1905, i, 455; 1906, i, 527, 980).—Since solanine from *Solanum sodomaeum* differs in composition from that extracted from *Solanum tuberosum*, the authors term it *solanine-s*.

On analysis, after being dried in a vacuum over potassium hydroxide and paraffin, *solanine-s* gives the formula  $(C_{27}H_{46}O_9N)_2 \cdot H_2O$ , which is confirmed by the analysis of various normal and basic salts and other derivatives, and also by investigation of its hydrolytic products.

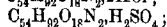
Carefully purified solanidine (see succeeding abstract) has the formula  $C_{18}H_{31}ON$ , and a study of the sugars also formed on hydrolysis of solanine shows that this change is represented thus:  $(C_{27}H_{46}O_9N)_2 \cdot H_2O + H_2O + H_2 = 2C_{18}H_{31}ON + C_6H_{12}O_6$  (galactose) +  $C_6H_{12}O_6$  (? dextrose) +  $C_6H_{12}O_5$  (? rhamnose). In estimating the methylpentose (? rhamnose) by conversion into methylfurfuraldehyde, and weighing this in the form of its phloroglucinol derivative, higher results than were expected were obtained, and, on investigation, it was found that the presence of certain sugars, such as galactose, diminishes, whilst that of others, namely, dextrose, increases markedly the yield of methylfurfuraldehyde.

The action of acetic anhydride on *solanine-s* yields a deca-acetyl-derivative,  $C_{54}H_{82}O_{18}N_2Ac_{10}$ , which yields solanine again on hydrolysis, whilst in the total products of hydrolysis of solanine, 16 atoms of hydrogen are replaceable by acetyl groups.

The action of nitrous acids on *solanine-s* (*loc. cit.*) gives a compound of the formula  $C_{54}H_{80}O_{18}N_2 \cdot HNO_3 \cdot 3H_2O$ , which does not behave as a salt, since treatment with alkali does not yield a basic compound. When heated gently with dilute acetic acid, this compound loses all its nitrogen (it is therefore named azosolanine), yielding a compound which has not been obtained crystalline, but has the formula  $C_{54}H_{80}O_{21} \cdot 2H_2O$  (*oxysolanol*). Treatment of solanine with a nitrite in hot aqueous acetic acid solution results in the formation of another nitrogen-free compound,  $C_{54}H_{88}O_{20} \cdot 2H_2O$ , which crystallises well, and is termed solanol. When heated with a dilute mineral acid, but these non-nitrogenous compounds undergo hydrolysis, yielding sugar

and other substances, which can also be obtained from solanidine; these substances are being investigated.

The following salts of solanine have been prepared: (1) Normal salts: the *hydrochloride*,  $C_{54}H_{92}O_{18}N_2 \cdot 2HCl$ ; the *sulphate*,



the *o-nitrobenzoate*,  $C_{54}H_{92}O_{18}N_2 \cdot 2NO_2 \cdot C_6H_4 \cdot CO_2H \cdot 8H_2O$ ; and the *picrate*,  $C_{54}H_{92}O_{18}N_2 \cdot 2OH \cdot C_6H_3(NO_2)_3$ . (2) Basic salts: the *hydrochloride*,  $C_{54}H_{92}O_{18}N_2 \cdot HCl$ ; the *hydrobromide*,  $C_{54}H_{92}O_{18}N_2 \cdot HBr$ ; and the *sulphate*,  $(C_{54}H_{92}O_{18}N_2)_2 \cdot H_2SO_4$ .

As has been indicated above, during hydrolysis solanine undergoes reduction, this being effected by the sugars formed. In fact, when heated with dextrose, solanine gives rise to a *dihydrosolanine*,  $C_{54}H_{94}O_{18}N_2 \cdot H_2O$ , which forms prismatic crystals, and may be the original product from which solanidine is formed.

*Deca-acetylsolanine* was not obtained crystalline, and may possibly be a mixture of deca- and undeca-acetyl derivatives.

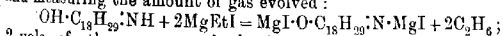
*Azsolanine* forms tufts of faintly green, silky needles, and in the anhydrous condition has the normal molecular weight in boiling *isoamyl* alcohol. It is a neutral compound, and gives neither the nitroso-reaction with phenol and sulphuric acid nor the *isonitroso*-reaction with a sulphuric acid solution of diphenylamine. When heated in a capillary tube it turns yellow, and contracts at  $230^\circ$ , blackens at  $275^\circ$ , and begins to melt at  $280^\circ$  without, however, completely fusing.

*Solanol* forms tufts of slender needles, which turn yellow at  $210^\circ$  and decompose at  $240$ — $245^\circ$ .

T. H. P.

**Solanidine sodomaeum.** V. GIUSEPPE ODDO (*Gazzetta*, 1911, 41, i, 534—552. Compare preceding abstract).—The author describes a new method of purifying solanidine. Thus obtained it has the formula  $C_{18}H_{31}ON$  when dried at  $105^\circ$  or  $3C_{18}H_{31}ON \cdot 2H_2O$  when dried under reduced pressure at the ordinary temperature. This new formula is confirmed by analysis of the various salts prepared (see below) and by a study of the hydrolysis of solanidine-s (*loc. cit.*).

When treated with acetic anhydride, solanidine-s gives a diacetyl derivative, which yields the base again on hydrolysis. The formation of this compound is best explained by supposing that the oxygen exists in the molecule in the form of hydroxyl and the nitrogen in a secondary state:  $OH \cdot C_{18}H_{29} \cdot NH$ . These functions of the oxygen and nitrogen atoms have been confirmed by treating solanidine-s (1 mol.) with magnesium ethyl iodide (3 mols.) in ethereal solution and measuring the amount of gas evolved:



2 vols. of ethane were evolved, whereas if the nitrogen atom were primary, 3 vols. should be obtained, if it were tertiary only 1 vol., due to the hydroxyl, and, if the latter were also missing, no ethane would be evolved. The iodo-magnesium compound thus obtained gives solanidine again when treated with water, and with acetyl chloride, it yields a diacetyl compound identical with that given by the action of acetic anhydride on the base.

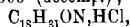
When solanidine-s is treated with sodium nitrite in presence of a

little acid, a compound is obtained which is similar to that given by solanidine-*s* (see preceding abstract), and is hence named azosolanidine. When treated with moderately concentrated acids, azosolanidine loses all its nitrogen, giving products which vary with the conditions of the action and are being investigated.

The formula given above for solanidine-*s* shows that this belongs to the series  $C_nH_{2n-4}$ . The lack of the six valencies necessary to make it a saturated compound is not due to the presence of double linkings in the molecule, since solanidine does not decolorise bromine in aqueous or chloroform solution, and only decolorises permanganate after some time. Solanidine-*s* must hence be regarded as a tricyclic compound.

[With EUGENIO FERRARI].—Solanidine-*s*, separated and purified by means of its hydrochloride, crystallises from alcohol in nacreous, white scales, m. p. 197—198°, and with concentrated sulphuric acid gives a reddish-yellow coloration, which, on addition of increasing proportions of water, becomes violet, green, and colourless.

[With GIOVANNI MONETA].—The following salts of solanidine-*s* were prepared: the *basic hydrochloride*,  $(C_{15}H_{31}ON)_3 \cdot 2HCl$ , forms silky, white needles, m. p. 302—303° (decomp.); the *hydrochloride*,

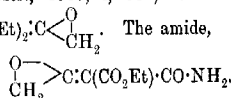


elongated prisms, turning yellow at about 250°, m. p. 291—292° (decomp.); the *hydrobromide*,  $C_{15}H_{31}ON \cdot HBr$ , elongated prisms, becoming decidedly yellow at 270°, m. p. 282—283° (decomp.); the *o-nitrobenzoate*,  $C_{15}H_{31}ON \cdot NO_2 \cdot C_6H_4 \cdot CO_2H$ , colourless, shining prisms, m. p. 222°; and the *picrate*,  $C_{15}H_{31}ON \cdot C_6H_3O_7N_3$ , quadrangular, shining prisms, which become orange-yellow on heating, m. p. 144—145°.

[With EUGENIO FERRARI].—*Diacetylsolanidine-s*,  $OAc \cdot C_{15}H_{29} \cdot NAc$ , was obtained only in the amorphous condition. The *iodomagnesium* compound gives solanidine when treated with water.

[With GIULIO BUZIO].—*Azosolanidine-s* form microscopic, regular, prismatic needles or rosettes of prismatic needles with a faint green tint, m. p. 260° (decomp.); its formula and the products its yields on heating with acids are being investigated. T. H. P

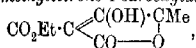
**Action of Halogeno-Fatty Acid Halides on Esters of Malonic Acid. II. Synthesis of Tetramic Acid.** ERICH BENARY (*Ber.*, 1911, 44, 1759—1765).—The substance,  $C_6H_{13}O_4$ , obtained as a by-product in the formation of ethyl tetrono-4-carboxylate from chloroacetyl chloride and ethyl sodiomalonate in warm ether (*Abstr.*, 1907, i, 381) is now shown to have the constitution  $C(CO_2Et)_2 \cdot C \begin{smallmatrix} O \\ \diagup \\ CH_2 \end{smallmatrix}$ . The amide,



obtained from it by the action of dry ammonia, is converted by an excess of boiling, alcoholic potassium hydroxide into a *potassium salt*,  $C_6H_5O_4NK_2$ , from which by acidification is obtained, *tetrame-*

4-carboxylic acid,  $\text{CO}_2\text{H}\cdot\text{C}\begin{smallmatrix} \text{C(OH)}\cdot\text{CH}_2 \\ \text{CO}-\text{NH} \end{smallmatrix}$ , decomp.  $214^\circ$ . This acid does not develop a coloration with alcoholic ferric chloride, and is easily decomposed by boiling water, yielding tetramic acid,  $\text{OH}\cdot\text{C}\begin{smallmatrix} \text{CH}-\text{CO} \\ \text{CH}_2\cdot\text{NH} \end{smallmatrix}$ , m. p.  $211^\circ$  (decomp.). Tetramic acid gives a blood-red coloration with ferric chloride, has only feeble acid properties, reduces warm ammoniacal silver nitrate, and develops a violet coloration with nitrous acid, due to the oximino-compound,  $\text{OH}\cdot\text{N}:\text{C}\begin{smallmatrix} \text{CO}\cdot\text{CH}_2 \\ \text{CO}\cdot\text{NH} \end{smallmatrix}$ , pale blue leaflets, decomp.  $205^\circ$ .

A by-product is not produced by the interaction of chloroacetyl chloride and methyl sodiomalonate in ether at  $0^\circ$ , methyl tetrone-4-carboxylate, m. p.  $188-189^\circ$  (decomp.), alone being produced. In a similar manner,  $\alpha$ -bromopropionyl bromide and ethyl sodiomalonate (2 mols.) yield ethyl 1-methyltetrone-4-carboxylate,



m. p.  $89-90^\circ$ , which is decomposed by dilute hydrochloric acid, forming methyltetroneic acid,  $\text{O}\begin{smallmatrix} \text{CO}-\text{CH} \\ \text{CMe}\cdot\text{C}\cdot\text{OH} \end{smallmatrix}$ , m. p.  $117-119^\circ$ , which develops red and violet colorations with ferric chloride and sodium nitrite respectively. C. S.

**Chromoisomerism of Pyridine, Quinoline, and Acridine Salts, and its Explanation by Valency Isomerism.** ARTHUR HANTZSCH (*Ber.*, 1911, 44, 1783-1828).—The existence of coloured modifications of certain pyridine, quinoline, and acridine salts has been explained at different times by the ionisation of chromophores (Decker, Abstr., 1904, ii, 702), by structural isomerism (Decker, Abstr., 1909, i, 408), or by polymerism (Hantzsch and Leupold, Abstr., 1909, ii, 198; Tinkler, Trans., 1909, 95, 921). The explanation, however, is not to be found in polymerism (compare this vol., i, 608), nor in structural isomerism in Decker's sense, but rather in the existence of chromoisomeric ammonium ions. The author quotes examples to prove that the polychromy of the salts in question, in the solid state, is independent of the nature of the anions and the cations, and in solutions is independent of the degree of association or of dissociation (in aqueous solution). The ultra-violet absorption spectra of polychromatic solutions of polychromatic salts differ greatly; even in one and the same solvent the absorption spectra vary enormously with the nature of the anion and with change of temperature or of concentration. This optical variability of polychromatic salts is in marked contrast to the optical constancy of the salts of cotarnine, the absorption spectra of which are practically identical in water, alcohol, or chloroform, and are independent of the nature of the anion. The absorption spectra show that the selective absorption of coloured ammonium salts is exclusively a property of the coloured ammonium ions, and that these organic chromophores are, in the absence of



chemical change, optically constant. It follows therefore that the solutions of the polychromatic pyridine, quinoline, *isoquinoline*, and acridine salts must, in consequence of their optical variability with the nature of the solvent or of the anion or with change of temperature or of concentration, contain, as chemically changeable chromophores, isomeric ammonium ions of different selective absorptive power; in other words, such solutions contain chromoisomeric ammonium salts. Only in certain limiting cases (as, for example, in the case of the cotarnine salts) do these solutions contain individual chromoisomerides; usually two or more chromoisomerides are present in equilibrium in the solution. The equilibrium of chromoisomeric ammonium halides is disturbed, in favour of the more strongly coloured chromoisomeride, by an increase in the associating power (or, better, by a decrease in the dissociating power) of the solvent, by an increase in the atomic weight of the halogen, and by an increase in the temperature or the concentration.

Since the solutions of a polychromatic salt (for example, 5-phenyl-10-methylacridonium sulphite) in different solvents are polychromatic, and the salt in the solid state occurs in differently coloured modifications, the polychromy is independent of a solvent and of the state of aggregation; moreover, since in solution the polychromy is referable to isomerism, the polychromy of the solid salts is also due to isomerism, not to association or polymorphism. This also follows from the genetic relation between polychromatic salt solutions and the solid salts, a relation manifested primarily by the identity of the colour of many salt solutions with that of the "solvates" (hydrates, alcoholates, chloroformates) separating therefrom. Several other phenomena are quoted to prove that the polychromy of solid pyridine, quinoline, and acridine salts is attributable to the existence of chromoisomerides.

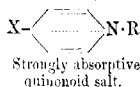
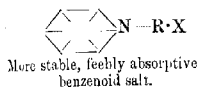
From the foregoing, the chromatropy (change of colour) of the solid salts naturally is due to chemical causes. It is a true intramolecular change of an unstable chromoisomeride into a more stable one, brought about, occasionally apparently spontaneously, more frequently by contact with a trace of a catalyst, especially with the vapours of those solvents which dissolve the chromatropic chromoisomerides with the same change of colour. The interconversions of the brown, red, yellow, and green modifications of 5-phenyl-10-methylacridonium sulphite, spontaneously or by contact with alcohol, ether, chloroform, nitrobenzene, or acetic acid, are tabulated. With regard to the number of individual chromoisomerides, it can be stated with considerable certainty in the case of the acridonium salts that the green, yellow, and red modifications are individual; all the other modifications are solid solutions or mixed salts of two, or even of all three, of these individuals.

The number of chromoisomeric salts in the pyridine, quinoline, and *isoquinoline* series cannot yet be stated with any degree of certainty, because these isomerides are much more labile than those of the acridine series, and can be isolated in the solid state only under exceptional circumstances. Apparently, however, there are two chromoisomerides in each series. One has a feeble absorbing power, and is represented by the almost colourless salts in the quinoline series, and by the quite

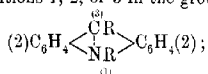
colourless salts of the pyridine series. The other chromoisomeride exhibits stronger selective absorption (the deep yellow to orange-red salts of the quinoline series, and the yellow salts of the pyridine series).

The salts of cotarnine and of neocotarnine also exhibit chromoisomerism (compare Salway, *Trans.*, 1910, 97, 1208). Cotarnine salts are especially interesting. Most of the salts with colourless anions (except the yellow iodide) are very faintly yellow in the solid state; in solution, all are intensely yellow and optically identical. This behaviour is explained by the existence of two chromoisomerides; one, feebly absorptive, is the predominating form in the solid salts, the other, strongly absorptive, is the only form stable in solution.

Chromoisomerides can be represented as valency isomerides in the light of Werner's theory of the constitution of ammonium salts. Of the four groups attached to the nitrogen atom one differs from the other three in being bound by a supplementary valency; the anion is attached to this unique group. The two chromoisomerides of the pyridine series (and in a similar manner those of the quinoline and isoquinoline series) can therefore be represented by the formulæ:



In the acridine series three formulæ are possible, according as the anion is linked at positions 1, 2, or 3 in the group



the yellow salts probably are benzenoid (anion in position 1), the green and the red salts quinonoid (anion in positions 2 and 3). The tendency to the formation of quinonoid instead of benzenoid salts is the greater the more unsaturated is the ring attached to the nitrogen atom; consequently, the quinonoid forms of chromoisomerides are rare in the pyridine series, occur somewhat frequently in the quinoline series, and are commonest in the acridine series.

Throughout the paper numerous examples are quoted in support of the statements made. Methods are described for the preparation of yellow, green, and red modifications of the salts of the acridine series. A few new compounds, such as the yellow, orange, and green modifications of 5-phenyl-10-methylacridonium thiocyanate, are described.

C. S.

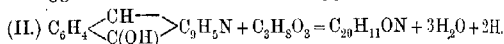
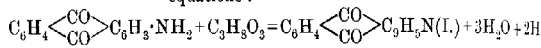
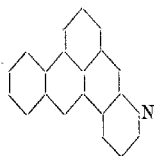
**Preparation of Indoxyl Derivatives.** GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 232780).—The action of carbonyl chloride on indoxyls (substituted or otherwise) is capable of a wide application, and leads to the production of crystalline derivatives in quantitative yield.

The compound,  $\text{C}_6\text{H}_4 \cdot \begin{array}{c} \text{N}(\text{COCl}) \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{CH}_2$ , is prepared by treating an ice-

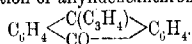
cold acid solution of indoxyl with carbonyl chloride, when the product separates out as a greyish-white, crystalline powder, m. p. 109–110°, its solution in concentrated sulphuric acid is yellow with a green fluorescence.

F. M. G. M.

**Action of Glycerol and Sulphuric Acid on Amino-compounds and on Compounds Free from Nitrogen Belonging to the Anthracene Group: Benzanthrone and Its Reduction Products. Observations on the Nomenclature of Complex Ring-Systems of the Anthracene Group.** OSCAR BALLY and ROLAND SCHOLL (*Ber.*, 1911, 44, 1656–1670).—The compound,  $C_{20}H_{11}ON$ , obtained by Bally (*Abstr.*, 1904, i, 237) by the action of sulphuric acid and glycerol on 1-aminoanthraquinone in the absence of an oxidising agent, is now found to be 3:4-pyridino-1:9-benzanthrone (annexed formula). With respect to the mechanism of the reaction, the authors consider that the first stage consists in the formation of  $\beta$ -anthraquinolinequinone (I.), which is then reduced to the anthranol derivative (II.), and finally converted by the further action of glycerol into pyridinobenzanthrone, according to the equations:



This view is supported by the fact that  $\beta$ -anthraquinolinequinone, on treatment with sulphuric acid and glycerol, yields pyridinobenzanthrone, and also by the behaviour of anthranol, which, when subjected to the same treatment, yields benzanthrone (Bally, *loc. cit.*). It is suggested that the formation of the latter compound is preceded by the intermediate formation of allylideneanthrone,

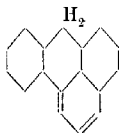


Benzanthrone may also be obtained from anthracene by the action of sulphuric acid and glycerol. In this case it is probable that benzanthrone is formed as an intermediate product.

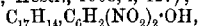
When reduced with alkaline hyposulphite or with zinc and aqueous sodium hydroxide, benzanthrone yields greenish-yellow solutions, which are considered to contain *dihydrobenzanthrone*,  $C_{17}H_{12}O$ .

*Benzanthrone* (annexed formula), prepared by distilling benzanthrone over zinc dust in a stream of hydrogen, crystallises in lustrous, pale yellow leaflets, m. p. 84°. It gives a red coloration with sulphuric acid, and dissolves in organic solvents with a green fluorescence. In solution it is oxidised rapidly by the air to benzanthrone. The *picrate*,  $C_{17}H_{10}C_6H_3(NO_2)_3OH$ , crystallises in slender, dark red needles, m. p. 110–111°.

10-*Dibromobenzanthrene*,  $C_{17}H_{10}Br_2$ , is obtained by brominating benzanthrone in glacial acetic acid solution; it forms yellow crystals, m. p. 174°.



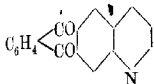
[With G. LENTZ].—When reduced with hydriodic acid and phosphorus, benzanthrone yields (1) a hydrocarbon,  $C_{34}H_{26}$  or  $C_{34}H_{30}$ , m. p. above  $320^\circ$ , and (2) dihydrobenzanthrene,  $C_{17}H_{14}$ , which crystallises in yellow needles, m. p.  $81^\circ$ , and gives green, fluorescent solutions (compare Liebermann and Roka, Abstr., 1908, i, 427); the *picrate*,



forms feather-shaped aggregates of lustrous, yellow needles, m. p.  $125^\circ$ .

Bromodihydrobenzanthrene,  $C_{17}H_{16}Br$ , prepared by brominating dihydrobenzanthrene in glacial acetic acid solution, crystallises in lustrous, colourless needles, m. p.  $123^\circ$ . Dibromodihydrobenzanthrene,  $C_{17}H_{14}Br_2$ , forms almost colourless needles, m. p.  $157^\circ$ .

2,3-Pyridinoanthraquinone [ $\gamma$ -anthraquinolinequinone] (annexed formula) is produced in small quantity in the preparation of 3:4-pyridino-1:9-benzanthrone from anthranol; it crystallises in yellow needles, m. p.  $322^\circ$ .



For details of the authors' proposed nomenclature of benzanthrone derivatives and allied compounds, the original must be consulted.

F. B.

**Quinaldinium Bases.** EDUARD VONGERICHTEN and W. ROTTA (*Ber.*, 1911, 44, 1419–1422. Compare Vongerichten and Höfchen, Abstr., 1908, i, 914).—The quinaldinium base obtained by the action of *N*-sodium hydroxide solution on 2-ethylquinoline ethiodide reacts in the cold with alkali and benzoyl chloride, yielding a green oil, a warm dilute acetic acid solution of which reacts with potassium iodide and yields a pale yellow, crystalline iodide,  $C_6H_4 \begin{smallmatrix} \text{NEt} \cdot \text{C} \cdot \text{CHBz} \\ | \\ \text{CH} = \text{CH} \end{smallmatrix}$ , with

m. p.  $197^\circ$ . This iodide does not give a coloration with alcoholic sodium hydroxide or with quinoline methiodide and sodium ethoxide. When boiled with concentrated hydrochloric acid in a reflux apparatus, the iodide yields benzoic acid, and on the addition of ammonia a base,

$C_6H_4 \begin{smallmatrix} \text{NEt} \cdot \text{C} \cdot \text{CHBz} \\ | \\ \text{CH} = \text{CH} \end{smallmatrix}$ , which crystallises from alcohol in golden-yellow

plates, m. p.  $139^\circ$ . The base dissolves in dilute acids, even acetic acid, yielding colourless solutions, but when warmed the acetic acid solution becomes deep yellow. When heated with hydrobromic acid at  $200^\circ$  for three hours and then made alkaline, the base yields an oil which with hydrochloric acid yields 1-ethylquinaldinium hydrochloride.

If *p*-chlorobenzoyl chloride is used instead of benzoyl chloride, the chlorinated base,  $C_{19}H_{16}ONCl$ , m. p.  $187^\circ$ , is obtained.

2-Methylquinoline methiodide and benzoyl chloride yield a product,  $C_{17}H_{11}ON$ , which crystallises in brilliant yellow needles, m. p.  $167-168^\circ$ .

The behaviour of 2-methylquinoline alkyl iodides with alkalis is thus entirely different from the reaction between quinoline alkyl iodides and alkalis, as in the latter case a rupture of the pyridine ring occurs (compare Kaufmann and Strübin, this vol., i, 321).

J. J. S.

**Preparation of Thiazole Compounds of "Thioindigo-Reds" and their Derivatives.** KALLE & Co. (D.R.-P. 233741).—The action of aldehydes and sulphur (or polysulphides) on the nitro- or amino-substituted 2-carboxymethylthiolbenzoic acids yields thiazole derivatives, which by oxidation and closing of the ring furnish "thiazole-thioindigo" derivatives. The product (a thiazole derivative of 2-carboxymethylthiolbenzoic acid) prepared from benzaldehyde and 4-nitro-2-carboxymethylthiolbenzoic acid forms yellow crystals, m. p. about 250°. F. M. G. M.

**holo- and meri-Quinonoid Salts of Benzidine.** WALTER MADELUNG (*Ber.*, 1911, 44, 1674—1676).—Mainly a reply to Piccard's criticism (this vol., i, 493) of previous work of the author (this vol., i, 323). F. B.

**Action of Hydrazine Hydrate on cycloHexanone.** NICOLAI M. KJNER and S. BELOFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 577—582).—cycloHexylidenehydrazine hydrate,  $C_6H_{10} \cdot N \cdot NH_2 \cdot H_2O$ , formed by the action of hydrazine hydrate on cyclohexanone, is a colourless liquid, b. p. 107—108°/28 mm.,  $D_4^{20}$  0.9866; on heating with dilute hydrochloric acid, it is resolved into its components, and on mixing with one or two vols. of water, it solidifies to a crystalline mass at 0°.

When reduced with absolute alcohol and sodium, the above compound yields: (1) cyclohexanol; (2) cyclohexylhydrazine,

$C_6H_{11} \cdot NH \cdot NH_2$ ,  
m. p. 46—50°, b. p. 195.5°/758 mm., and gives a silver mirror with ammoniacal silver nitrate solution in presence of alkali; it gives the thioureide,  $NHPh \cdot CS \cdot NH \cdot NH \cdot C_6H_{11}$ , m. p. 143—143.5°, and with pyruvic acid forms the cyclohexylhydrazone of the acid,

$CO_2H \cdot CMe \cdot N \cdot NH \cdot C_6H_{11}$ ,  
m. p. 110—112°; on oxidation with potassium ferricyanide it yields cyclohexane.

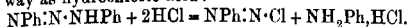
cycloHexylideneazine,  $C_6H_{10} \cdot N \cdot N \cdot C_6H_{10}$ , also obtained by the interaction of hydrazine nitrate and cyclohexanone, forms rhombic plates, m. p. 33.5—34°, b. p. 175°/28 mm.; the liquid remains supercooled for a long time, and has  $D_4^{20}$  0.9847,  $n_D^{20}$  1.5268.

Dicyclohexylhydrazine,  $NH_2 \cdot N(C_6H_{11})_2$ , obtained by reducing the preceding compound, has b. p. 220—260°, and gives a hydrochloride,  $C_{12}H_{25}N_2Cl$ . This compound is probably formed by isomerisation of the s-compound,  $NH \cdot C_6H_{11} \cdot NH \cdot C_6H_{11}$ , which should be given by the reduction of the azine. T. H. P.

**Relations of  $\alpha$ -Benzaldehydephenylhydrazone to Certain Nitrogen Compounds.** ROBERTO CRUSA and UGO PESTALOZZA (*Gazzetta*, 1911, 41, i, 391—395).—The aim of the authors' experiments was to ascertain if any analogy is shown between the chemical behaviour of the more stable or  $\alpha$ -form of benzaldehydephenylhydrazone, m. p. 156°, and that of the stable diazoaminobenzene, m. p. 96°, which may be regarded as the phenylhydrazone of nitrosobenzene.

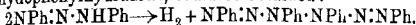
With the latter, picric acid and picryl chloride in benzene solution give the respective intensely brown additive compounds, as is the case with phenylhydrazones of aromatic aldehydes, but these are almost

always unstable. In 96% alcohol the action of picric acid (1 mol.) on diazoaminobenzene (1 mol.) yields immediately a brown, powdery precipitate (? the picrate), which, in a few minutes, undergoes transformation into diazobenzene picrate, so that picric acid here acts in the same way as hydrochloric acid:



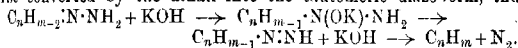
This action affords a convenient and rapid method of preparing diazobenzene picrate.

The actions of amyl nitrate and of mercuric oxide on diazoaminobenzene were studied to see if an oxidation product containing a chain of six nitrogen atoms, and analogous to that formed by benzaldehydephenylhydrazone, could be obtained:



With amyl nitrate the reaction is very complex, the only product identified being diazobenzene nitrate; with mercuric oxide the latter is not reduced, the mercury salt of diazoaminobenzene being formed. This different behaviour of diazoaminobenzene from that of benzaldehydephenylhydrazone is in agreement with the acid character of the former and the feebly basic nature of the hydrazones. T. H. P.

**Catalytic Decomposition of Alkylidenehydrazines as a Method of Obtaining Hydrocarbons.** NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 582—595).—When an alkylidenehydrazine is heated in presence of a large quantity of solid potassium hydroxide, the base decomposes as follows:  $\text{C}_n\text{H}_{m-2}\cdot\text{N}\cdot\text{NH}_2 = \text{C}_n\text{H}_m + \text{N}_2$ , these products being the same as are obtained by the oxidation of the primary hydrazines by means of potassium ferricyanide in an alkaline solution. The alkylidenehydrazine is probably first converted by the alkali into the tautomeric diazo-form, thus:



In this way 1-methylcyclohexylidene-3-hydrazine gives a yield of 54% of methylcyclohexane, and thujylidenehydrazine, of 70% of thujane.

*Camphylidenehydrazine* (annexed formula), prepared by boiling camphor and hydrazine hydrate in alcoholic solution, forms a white, crystalline mass, m. p. 53—55°,  $[\alpha]_D - 40.81^\circ$  (in ether),  $-32.74^\circ$  (90% alcohol), and yields a liquid hydrate soluble in water. Its hydrochloride,  $\text{C}_{10}\text{H}_{16}\cdot\text{N}\cdot\text{NH}_2\cdot\text{HCl}$ , m. p. 180°,  $[\alpha]_D - 31.33^\circ$  (water),

was prepared. When hydrolysed with excess of hydrochloric acid, it is completely converted into camphor and hydrazine hydrochloride, but when 1 mol. of the acid is used per 1 mol. of the camphylidenehydrazine, in addition to camphor, a considerable quantity of camphanazine (compare Angeli and Castellana, *Atti R. Accad. Lincei*, 1905, [v], 14, i, 669—677) is also obtained:  $\text{C}_{10}\text{H}_{16}\cdot\text{N}\cdot\text{NH}_2\cdot\text{HCl} + \text{C}_{10}\text{H}_{16}\text{O} = \text{C}_{10}\text{H}_{16}\cdot\text{N}\cdot\text{N}\cdot\text{C}_{10}\text{H}_{16} + \text{H}_2\text{O} + \text{HCl}$ ; camphanazine has the rotations,  $[\alpha]_D = -92.33^\circ$  (benzene),  $-90.06^\circ$  (ether),  $-37.27^\circ$  (methyl alcohol),  $-19.25^\circ$  (ethyl alcohol), and  $-14.18^\circ$  (propyl alcohol).

When heated with potassium hydroxide, camphylidenehydrazine (30 grams) yields camphane (10 grams).

[With A. PROSKURJAKOFF].—*Fenchane* (annexed formula), obtained together with fenchanazine (see below) by heating fenchylidenehydrazine (from fenchone and hydrazine hydrate) with dry potassium hydroxide, is a mobile liquid with a faint camphor-like smell, b. p. 151.5°/763 mm.,  $D_4^{20}$  0.8326,  $n_D^{20}$  1.4463,  $[\alpha]_D^{20}$  -16.33°; it does not react with perman-

ganate, bromine, boiling fuming nitric acid, or fuming hydriodic acid in a sealed tube at 210°.

*Fenchanazine*,  $C_{10}H_{16} \cdot N \cdot N \cdot C_{10}H_{16}$ , forms oblique, quadrangular plates, m. p. 106°,  $[\alpha]_D^{20}$  +212.9°, and is converted into fenchone and hydrazine hydrochloride on heating with concentrated hydrochloric acid.

When heated with solid potassium hydroxide, *cyclohexylidenehydrazine hydrate* yields *cyclohexane*,  $C_6H_{10} \cdot N \cdot NH_2 \cdot OH = C_6H_{11} + N_2 + H_2O$ , and *cyclohexanol*,  $2C_6H_{10} \cdot N \cdot NH_2 \cdot OH = 2C_6H_{11} \cdot OH + N_2 + N_2H_4$ . T. H. P.

**Quaternary Ammonium Chlorides from Diphenyl Carbamide Chloride and Pyridine or Quinoline.** JOHANNES HEINZOG and K. BUDY (*Ber.*, 1911, 44, 1584—1594).—Acid chlorides in presence of tertiary bases are converted into acid anhydrides by means of water or sodium carbonate. It is now found that sodium or potassium hydroxide is even more efficient at 0° in facilitating this change. The additive compound of diphenylcarbamide chloride and pyridine is thus readily converted into *diphenylcarbamic anhydride*,  $(NPh_2 \cdot CO)_2O$ , which forms yellow crystals, m. p. 121—123°.

In addition a yellow, crystalline quaternary base, *diphenylcarbamyropyridinium hydroxide*, m. p. 189°, is obtained. This base is remarkable in being neutral, soluble in organic solvents, but insoluble in water; when hydrolysed by boiling with acetic and hydrochloric acids, diphenylcarbamide and glutacetaldehyde are formed, the latter being identified as Zincke's dianilide. Accordingly, the base has the composition:  $NPh_2 \cdot CO \cdot N^+ \cdot CH \cdot CH^+ \cdot CH \cdot CH^+ \cdot CH \cdot OH$ .

*Diphenylcarbamyloquinolinium chloride*, obtained by the interaction of the components in sunlight, forms red crystals, m. p. 135—137°. The *platinichloride* separates in yellow crystals, m. p. 232°. This reacts quite differently with sodium hydroxide; diphenylcarbamic acid is not formed, the sole product of the reaction being *C-hydroxy*-

*N-diphenylcarbamyldihydroquinoline*,  $C_6H_4 \begin{matrix} < CH \\ & \backslash \\ & N(CO \cdot NPh_2) \end{matrix} > CH \cdot OH$ ,

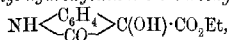
a reddish-white, amorphous powder. The *ethyl ether* forms long faintly yellow-coloured needles, m. p. 195° (quickly heated); the *methyl ether* crystallises in yellow needles, m. p. 160—162°. Both ethers on boiling with 10% hydrochloric acid are converted into diphenylcarbamyloquinolinium chloride. E. F. A.

**Dehydroindigotin. III. Decomposition by means of Acid and Alkalis.** LUDWIG KALB (*Ber.*, 1911, 44, 1455—1464. *Compar. Abstr.*, 1909, i, 966, 967; 1910, i, 340).—Dilute mineral acids react

with dehydroindigotin in two different ways: (1) Two molecules of water react with one of dehydroindigotin, yielding equimolecular quantities of dioxindole and isatin. (2) Two molecules of water react with two of the compound, yielding one molecule of indigotin and two of isatin. The second is the chief reaction when dehydroindigotin is boiled with water (compare O'Neill, *Chem. News*, 1892, 65, 124; Marchlewski and Radcliffe, *Abstr.*, 1899, i, 74). The dioxindole and isatin react to form isatyde (Heller, *Abstr.*, 1904, i, 416), a good yield of which can be obtained by shaking dehydroindigotin acetate for sixteen hours with a mixture of concentrated hydrochloric acid and water (2:1).

Di-isatic acid (Marchlewski and Radcliffe, *loc. cit.*), prepared by the action of sodium hydroxide solution on dehydroindigotin, is decomposed when warmed for two hours at 85° with 10% potassium hydroxide solution, yielding anthranilic acid, dioxindole, and carbon dioxide.

The formula  $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}(\text{OH}) \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$  is suggested for di-isatic acid, and during its formation molecular rearrangement occurs. Hydrocyanoisatin when hydrolysed with alcoholic hydrochloric acid yields *ethyl hydroxyoxindole-3-carboxylate*,



which crystallises from water in hexagonal plates, m. p. 152°. The same ester is also formed by the action of 2*N*-sodium carbonate solution on ethyl indoxanthinate, a reaction which involves a molecular rearrangement similar to that which occurs in the formation of di-isatic acid. The reaction between alkalis and dehydroindigotin is regarded as consisting first of all in the addition of water, yielding a dihydroxyindigo-white. This by a wandering of oxygen atoms undergoes decomposition into indigotin and 2-hydroxyindoxyl-2'-carboxyanilide-2-carboxylic acid; the greater part of the latter then passes over into di-isatic acid, whilst the smaller portion is decomposed, yielding anthranilic acid, dioxindole, and carbon dioxide. J. J. S.

**Indigo-Yellow.** BERTHOLD WUTH (*Chem. Zeit.*, 1911, 73, 667).—When heated with excess of benzoyl chloride, indigotin yields dibenzoylindigotin. In the presence of condensing agents, such as metals and metallic chlorides, however, the reaction proceeds differently. Only one molecule of benzoyl chloride is used, and a hitherto unknown compound of intense yellow colour is produced, crystallising from nitrobenzene in greenish-yellow needles (m. p. 275–277°). Unlike dibenzoylindigotin, it cannot be re-converted into indigotin by saponifying agents. It follows that substitution takes place at the imino-groups, and that inner condensation occurs with the formation

of a new ring, thus:  $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} \text{---} \text{C} \text{---} \text{C}_6\text{H}_4 \\ | \qquad \quad | \\ \text{CO} \text{---} \text{N} \cdot \text{CPh} \cdot \text{N} \cdot \text{CO} \end{array}$

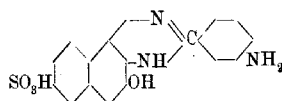
But whether the spare carbon valency is saturated by hydrogen or hydroxyl or by one of the indigo-nitrogens is not yet decided. Determination of the molecular weight by the boiling-point method points to the empirical formula  $\text{C}_{23}\text{H}_{14}\text{O}_2\text{N}_2$ .



Substitution products of indigotin, such as di-bromo-indigotin, react similarly with benzoyl chloride. Yellow condensation products are likewise obtained by replacing benzoyl chloride by its nuclear substitution products, or by benzotrichloride, benzylidene chloride, and similar substances. The compounds produced have the characteristic qualities of the vat dyes, and gives rise to greenish-yellow shades.

The above-described compound is the indigo-yellow 3G-Ciba of commerce. J. D. K.

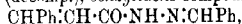
[Preparation of 4-Hydroxy-2-*m*-aminophenyl- $\alpha$ -naphthiminazole-7-sulphonic Acid.] LEOPOLD CASSELLA & Co. (D.R.P. 233939).—4-Hydroxy-2-*m*-aminophenyl- $\alpha$ -naphthiminazole-7-sulphonic acid (annexed formula) is prepared by the condensation of 3:4-diamino-



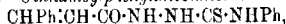
$\beta$ -naphthol-7-sulphonic acid with aminobenzaldehyde bisulphite; its sodium salt is crystalline and sparingly soluble in water. When coupled with diazotised aniline in alkaline solution, it yields a red aminoazo-derivative, and the properties of numerous valuable direct cotton dyes obtained when it is combined with diazo- and bisdiazo-compounds are described in the patent.

F. M. G. M.

Formation of 1-Nitroso-5-phenyl-3-pyrazolidone from Cinnamoyl Hydrazide. ERNST MUCKERMANN (*J. pr. Chem.*, 1911, [ii], 83, 513—540).—Hydrazides of monobasic unsaturated acids have been hitherto unexamined. The present work deals with cinnamoylhydrazide,  $\text{CHPh:CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ , m. p. 101°, which is readily obtained by boiling ethyl cinnamate with alcohol and hydrazine hydrate. It exhibits the usual reducing properties of primary acid hydrazides, yields dicinnamoylhydrazide,  $\text{N}_2\text{H}_2(\text{CO}\cdot\text{CH:CHPh})_2$ , m. p. 217—248°, by boiling with alcoholic iodine, and forms a hydrochloride, m. p. 201° (dec. mp.), benzylidene compound,



m. p. 180°, benzoyl derivative, m. p. 158—159°, and condensation products with acetone,  $\text{CHPh:CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{N:CM}_2$ , m. p. 137°, and with ethyl acetoacetate,  $\text{CHPh:CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{N:CM}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , m. p. 125—126°. Its hydrochloride reacts with aqueous potassium cyanate to form cinnamoylsemicarbazide,  $\text{CHPh:CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , m. p. 161—162°. Cinnamoylphenylthiosemicarbazide,



from cinnamoylhydrazide and alcoholic phenylthiocarbimide, has m. p. 146°.

Aqueous cinnamoylhydrazide hydrochloride reacts with sodium nitrite at 0° to form, not the expected azoimide, but a yellow substance,  $\text{C}_9\text{H}_9\text{O}_2\text{N}_3$ , m. p. 127—128° (decomp.), which is a nitroso-compound, but not a hydrazide on account of its strongly acid nature and absence of reducing properties. Its acid properties indicate the presence of the group  $\text{NH}\cdot\text{CO}$ , and the constitution, 1-nitroso-5-phenyl-3-pyrazolidone,

$\text{CH}_3\cdot\text{CHPh} > \text{N}\cdot\text{NO}$ , is supported by the following evidence (compare also Knorr, Abstr., 1887, 665; von Rothenburg, *ibid.*, 1895, i, 302). Its ammonium salt,  $\text{C}_9\text{H}_9\text{O}_2\text{N}_3\cdot\text{NH}_4$ , m. p.  $147^\circ$  (decomp.), obtained from the nitrosophenylpyrazolidon- and 10% ammonia, is easily converted into the silver salt,  $\text{C}_9\text{H}_9\text{O}_2\text{N}_3\cdot\text{Ag}$ , m. p.  $144-145^\circ$ , barium salt,  $(\text{C}_9\text{H}_9\text{O}_2\text{N}_3)_2\cdot\text{Ba}\cdot\text{H}_2\text{O}$ , greenish-blue copper salt,  $(\text{C}_9\text{H}_9\text{O}_2\text{N}_3)_2\cdot\text{Cu}\cdot 2\text{H}_2\text{O}$ ,

and picrate,  $\text{C}_9\text{H}_9\text{O}_2\text{N}_3\cdot\text{NH}_4\cdot\text{C}_6\text{H}_3(\text{NO}_2)_3\cdot\text{OH}$ , m. p.  $127^\circ$ ; from the silver salt ethereal ethyl iodide produces 1-nitroso-5-phenyl-2-ethyl-3-pyrazolidone, m. p.  $98^\circ$ . The nitrosophenylpyrazolidone yields with bromine and glacial acetic acid at  $0^\circ$  von Rothenburg's 4:4-dibromo-3-phenyl-5-pyrazolone (Abstr., 1895, i, 686). 1-Nitroso-5-phenyl-3-pyrazolidone is converted by boiling concentrated hydrochloric acid into cinnamic acid, by cold concentrated hydrochloric acid into  $\beta$ -chlorodihydrocinnamic acid (?), and by boiling dilute sulphuric acid, D 1.06, into von Rothenburg's 4-oximino-3-phenyl-5-pyrazolone (*loc. cit.*).

C. S.

**Preparation of 5:5-Dialkylthiobarbituric Acids.** EMANUEL MERCK (D.R.-P. 234012).—The preparation of 5:5-dialkylbarbituric acids by means of carbamide has previously been described (Abstr., 1904, i, 380), and the results obtained by substituting thiocarbamide in the reaction are now recorded

Diethylthiobarbituric acid,  $\begin{array}{c} \text{NH}\cdot\text{CO}\cdot\text{CEt}_2 \\ | \\ \text{CS}\cdot\text{NH}\cdot\text{CO} \end{array}$ , yellow tablets or needles, m. p.  $180^\circ$ , is prepared by heating ethyl diethylmalonate with thiocarbamide in alcoholic sodium ethoxide solution at  $105^\circ$  with continual stirring.

Dipropylthiobarbituric acid, glistening leaflets, m. p.  $154^\circ$ , can be converted by removal of sulphur into dipropylbarbituric acid, m. p.  $145^\circ$ . F. M. G. M.

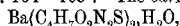
**Synthesis of Thiohydantoin.** SHIGERU KOMATSU (*Mem. Coll. Sci. Eng.*, 1911, 3, 1—12).—The author has succeeded in preparing the previously unknown thiocarbamide form of thiohydantoin from glycine and potassium thiocyanate at  $100^\circ$ , using acetic anhydride as a catalyst. Thiohydantoinic acid is first formed, and this loses  $\text{H}_2\text{O}$  on heating with hydrochloric acid on the water-bath, leaving the compound referred to. Similarly,  $\alpha$ -alanine yields  $\alpha$ -5-methylthiohydantoin.

Thiohydantoinic acid,  $\text{NH}_2\cdot\text{CS}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , forms colourless needles, m. p.  $170-171^\circ$  (dec. mp.).

Thiohydantoin,  $\text{S}\cdot\text{C} < \begin{array}{c} \text{NH}\cdot\text{CO} \\ | \\ \text{NH}\cdot\text{CH}_2 \end{array}$ , forms colourless needles, decomposing on heating. When heated with hydrochloric acid in sealed tubes at  $160^\circ$ , it is decomposed into glycine, carbon dioxide, hydrogen sulphide, and ammonium chloride. It is not hydrolysed to thioglycollate like Volhard's isothiocarbamide form of this hydantoin. The potassium salt,  $\text{SK}\cdot\text{C} < \begin{array}{c} \text{N}\cdot\text{CO} \\ | \\ \text{NH}\cdot\text{CH}_2 \end{array}$ , forms a colourless, crystalline precipitate.

*2-Methylthiohydantoin*,  $\text{SMe} \cdot \text{C} \begin{smallmatrix} \text{N} \text{---} \text{CO} \\ \text{NH} \text{---} \text{CH}_3 \end{smallmatrix}$ , prepared by heating the potassium salt of thiohydantoin with excess of methyl iodide on the water-bath, forms colourless needles, soon darkening when kept. When fused with potassium hydroxide and acidified, it gives the odour of mercaptan.

*r-α-Methylthiohydantonic acid*,  $\text{NH}_2 \cdot \text{CS} \cdot \text{NH} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$ , forms colourless needles, m. p. 164—165°. The barium salt,

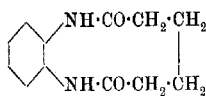


is very hygroscopic, m. p. about 100°.

*r-5-Methylthiohydantoin*,  $\text{S} \cdot \text{C} \begin{smallmatrix} \text{NH} \text{---} \text{CO} \\ \text{NH} \text{---} \text{CHMe} \end{smallmatrix}$ , prepared from *r-α-methylthiohydantonic acid*, forms pearly scales, m. p. 158°. By treating the hot aqueous solution of *r-5-methylthiohydantoin* with mercuric oxide, *r-5-methylhydantoin* (Urech, Abstr., 1873, 380) is obtained.

J. D. K.

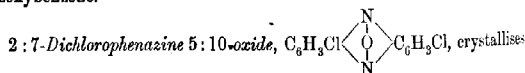
**A Group of Synthetic Organic Colloids.** EDGAR WEDFRIND (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 303—304).—By the action of adipyl chloride on *o*-diamines of the benzene series, amorphous substances are obtained which contain a ring of ten atoms (unrearranged formula). These substances are typical colloids, are insoluble in most solvents except acetic acid, and cannot be obtained in crystalline form. Colloidal solutions



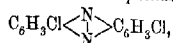
can be prepared by pouring acetic acid solutions into water or by triturating with potassium hydroxide solution, and afterwards treating with successive quantities of distilled water. Opalescent, milky liquids are thus obtained, which can be purified by dialysis, and exhibit all the properties of colloidal solutions. The solutions are coagulated by electrolytes, and much less readily by freezing. The possibility of obtaining these substances in colloidal form by the trituration method is supposed to be connected with their acid amide character.

H. M. D.

**Behaviour of Certain Para-substituted Nitrosobenzenes towards Sulphuric Acid.** EUGEN BAMBERGER and W. HAN (*Annalen*, 1911, 382, 82—128. Compare Bamberger, Busdorf, and Sand, Abstr., 1898, i, 521).—By allowing a glacial acetic acid solution of *p*-chloronitrosobenzene to drop slowly into well stirred concentrated sulphuric acid kept at 20—24°, the chief products are 2:7-dichlorophenazine-5:10-oxide, which is insoluble in dilute alkalis and in alcohol. 4'-chloro-4-nitrosodiphenylhydroxylamine, which is soluble in dilute alkalis, unaltered *p*-chloronitrosobenzene, and 4:4'-dichloro-azoxybenzene.

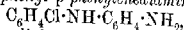


from glacial acetic acid in pale golden-yellow, lustrous needles, m. p. 237.5–238° (decomp.), when rapidly heated. As a rule, it has an orange-brown colour, but this is changed to the characteristic golden-yellow after being twice treated with fuming nitric acid at the ordinary temperature. Its solution in concentrated sulphuric acid has a blood-red colour, and when reduced with stannous chloride and hydrochloric acid, it yields 2:7-dichlorophenazine,



which crystallises from glacial acetic acid or xylene in glistening, lemon-yellow needles, m. p. 265.5°. Its solution in concentrated sulphuric acid is red; when moistened with concentrated hydrochloric acid it turns red, but with more acid it dissolves, yielding a yellow solution. Its alcoholic solution reacts with an alcoholic solution of silver nitrate, yielding slender, moss-green needles with a bronzy lustre. 2:7-Dichlorophenazine-5:10-oxide can be synthesised by heating *p*-chloroaniline, *p*-chloronitrobenzene, and dry sodium hydroxide for five hours at 110–120° (compare Wohl and Aue, Abstr. 1901, i, 612), but an appreciable amount of 4:4'-dichloroazobenzene is formed at the same time.

4'-Chloro-4-nitrosodiphenylhydroxylamine,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{N}(\text{OH}) \cdot \text{C}_6\text{H}_4 \cdot \text{NO}$ , crystallises from acetone in greenish-yellow plates with a pronounced bronzy lustre, and has m. p. 143° (decomp.); it dissolves in alkalis and also in concentrated sulphuric acid, yielding red solutions, and when reduced with zinc dust and boiling 2*N*-ammonium chloride solution yields 4'-chlorophenyl-*p*-phenylenediamine,

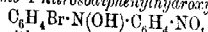


which crystallises from light petroleum in glistening, flat needles, m. p. 66.5–67°, only sparingly volatile in steam. The hydrochloride forms colourless, glistening crystals, and the sulphate is sparingly soluble. When the hydroxylamine derivative is reduced with zinc dust and hot 2*N*-hydrochloric acid, *p*-chloroaniline is also formed.

The formation of chloronitrosodiphenylhydroxylamine from *p*-chloronitrobenzene and concentrated sulphuric acid is accompanied by the elimination of an atom of chlorine in the form of hydrogen chloride.

Under specific conditions it is possible to obtain appreciable amounts of *p*-chloronitrobenzene by the action of concentrated sulphuric acid on the corresponding nitroso-compound.

*p*-Bromonitrosobenzene reacts with concentrated sulphuric acid in much the same manner as its chlorinated analogue. 2:7-Dibromophenazine 5:10-oxide,  $\text{C}_{12}\text{H}_6\text{ON}_2\text{Br}_2$ , crystallises from glacial acetic acid or xylene in glistening, red needles, or after treatment with fuming nitric acid in golden-yellow needles, m. p. 240°, and on reduction with stannous chloride and hydrochloric acid yields 2:7-dibromophenazine,  $\text{C}_{12}\text{H}_6\text{N}_2\text{Br}_2$ , which crystallises from glacial acetic acid in orange-yellow or golden-yellow needles, m. p. 244.5–245°. 4'-Bromo-4-nitrosodiphenylhydroxylamine,



is formed together with a dibromo-derivative, and after repeated

fractional solution in ammonium hydroxide, fractional precipitation with dilute hydrochloric acid, and crystallisation from a mixture of acetone and light petroleum, is obtained as a yellow powder with m. p. 155°. On reduction with zinc and ammonium chloride solution it yields 4'-bromophenyl-*p*-phenylenediamine,  $C_6H_4Br \cdot NH \cdot C_6H_4 \cdot NH_2$ , which crystallises from light petroleum in glistening, pale yellow needles, m. p. 75.5–76°. The sulphate,  $2C_{12}H_{11}N_2Br \cdot H_2SO_4$ , is very sparingly soluble, and has m. p. 229°.

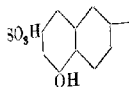
Dibromonitrosodiphenylhydroxylamine,  $C_6H_4Br \cdot N(OH) \cdot C_6H_4 \cdot NO$ , has m. p. 130°. The amounts of the various products obtained from 42 grams of *p*-bromonitrosobenzene were: dibromophenazine oxide, 8.2; dibromophenazine, 0.3; bromonitrosodiphenylhydroxylamine, 5.0; dibromonitrosodiphenylhydroxylamine, 1.4; and red crystals,  $C_6H_4Br \cdot NO$ , 1.5 grams.

*p*-Iodonitrosobenzene forms glistening, grass-green needles, m. p. 103.5–104.5° (compare *Ber.*, 1895, 28, 249), and is accompanied by 4:4'-di-iodoazobenzene. *p*-Iodophenylhydroxylamine begins to sinter at 70°, but is not completely molten at 145°, and by-products obtained in its formation are 4:4'-di-iodoazoxybenzene, m. p. 207–208° (Gabriel, this Journ., 1877, i, 307, gives 199–199.5°), and a substance with m. p. 214–215°, which is probably an isomorphous mixture of di-iodoazobenzene and di-iodoazoxybenzene. 2:7-Di-iodophenazine 5:10 oxide,  $C_{12}H_6ON_2I_2$ , crystallises from xylene in glistening, brownish-yellow needles, m. p. 241° (decomp.), and when reduced yields 2:7-di-iodophenazine,  $C_{12}H_6N_2I_2$ , which crystallises in glistening, yellow needles, m. p. 235°. 4-Iodo-4-nitrosodiphenylhydroxylamine,  $C_6H_4I \cdot N(OH) \cdot C_6H_4 \cdot NO$ , crystallises from acetone in glistening, greenish-yellow plates, m. p. 150–150.5° (decomp.), and is very sparingly soluble in ammonium hydroxide solution. Di-iodonitrosodiphenylhydroxylamine,  $C_6H_4I \cdot N(OH) \cdot C_6H_4I \cdot NO$ , crystallises from acetone in brownish-yellow nodules, m. p. 157° (decomp.), and is soluble in alkalis and ammonium hydroxide solution. Small amounts of lustrous, bright red plates, m. p. 188.5°, and of glistening, orange-red or yellow crystals, m. p. 240°, are also obtained by the action of concentrated sulphuric acid on *p*-iodonitrosobenzene. The amounts of products from 45 grams of *p*-iodonitrosobenzene were: *p*-iodonitrosobenzene, 0.07; di-iodophenazine oxide, 7.1; iodonitrosodiphenylhydroxylamine, 2.5; di-iodonitrosodiphenylhydroxylamine, 0.4; red plates, m. p. 188.5°, 0.4; and product, m. p. 240°, 0.05 grams.

Twenty grams of *p*-nitrosotoluene when treated with concentrated sulphuric acid in the presence of glacial acetic acid gave: dimethylphenazine oxide, 4; dimethylphenazine, 0.95; *p*-azoxytoluene, 0.55; *p*-azotoluene, 0.05; mixture of azo- and azoxy-compounds, 0.5; an amorphous, dark brown powder, 6.5, and pale red powder, 2.1 grams.

2:7-Dimethylphenazine 5:10-oxide,  $C_{14}H_{12}ON_2$ , crystallises in glistening, pale gold-n-yellow needles, m. p. 204–205°. The hydrochloride and sulphate form orange-yellow, glistening needles, which are hydrolysed by water. 2:7-Dimethylphenazine,  $C_{14}H_{12}N_2$ , crystallises from alcohol in pale yellow, glistening needles, m. p. 162.5–163°, and yields a sulphate in the form of golden-yellow needles. J. J. S.

**Preparation of Hydroxy- $\beta$ -naphthylpyrazolonemonosulphonic Acids.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.P. 233068).—When the  $\beta$ -naphthylpyrazolonedisulphonic acids (prepared from  $\beta$ -naphthylhydrazinedisulphonic acids and ethyl acetoacetate) are fused with potassium hydroxide at 160–180°, they yield the corresponding hydroxy-naphthylpyrazolonemonosulphonic acids.



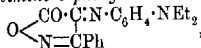
5'-Hydroxy- $\beta$ -naphthyl-3-methyl-5-pyrazolone-7-sulphonic acid (annexed formula), a colourless, crystal-

line powder, was thus prepared from 1- $\beta$ -naphthyl-5':7'-disulphonyl-3-methyl-5-pyrazolone; it furnishes a yellow nitroso-derivative.

F. M. G. M.

**Azomethines derived from Phenylisooxazolone.** ANDRÉ MEYER (*Compt. rend.*, 1911, 152, 1677–1680. Compare Abstr., 1908, i, 368).—A description of new compounds analogous to that previously obtained by the condensation of phenylisooxazolone with nitrosodimethylaniline. The substances all melt with decomposition, are decomposed by alkalis, and develop a violet coloration with sulphuric acid.

4-Diethylaminophenylimino-3-phenylisooxazolone,

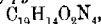


steel-grey prisms, m. p. 117°; the methylethylamino-compound forms violet needles, m. p. 143°; the anilino-derivative,  $\text{C}_{21}\text{H}_{15}\text{O}_2\text{N}_3$ , has m. p. 141–142°.

Phenylisooxazolone also condenses with nitrosopyrazoles, giving red or brown compounds of the type  $\text{O} \begin{array}{c} \diagup \text{CO} \cdot \text{C} \cdot \text{N} \cdot \text{C} = \text{CR} \\ \diagdown \text{N} = \text{CPh} \text{CMe} = \text{N} \end{array} \text{NR}'$ .

Their solutions in acetic acid or alcohol are violet, but become colourless through hydrolysis.

3:5-Dimethylpyrazoleimino-3'-phenylisooxazolone,  $\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_4$ , m. p. 140°. 1-Phenyl-3:5-dimethylpyrazoleimino-3'-phenylisooxazolone,

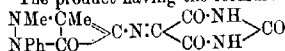


m. p. 99°. 1:5-Diphenyl-3-methylpyrazoleimino-3'-phenylisooxazolone,  $\text{C}_{25}\text{H}_{18}\text{O}_2\text{N}_4$ , m. p. 143–144°.

Nitrosoantipyrene condenses with phenylisooxazolone, giving the

compound  $\text{O} \begin{array}{c} \diagup \text{CO} \cdot \text{C} \cdot \text{N} \cdot \text{CH} \cdot \text{CO} \\ \diagdown \text{N} = \text{CPh} \text{CMe} = \text{N} \end{array} \text{NPh}$ , m. p. 147–148°. The corre-

sponding tolyl derivative has m. p. 152°. The two foregoing substances are somewhat analogous to purpuric acid, if the latter has the constitution ascribed to it by Slimmer and Stieglitz (Abstr., 1904, i, 634). For the purpose of comparison, alloxan was condensed with aminoantipyrene. The product having the formula



resembles murexide in appearance and solubility, and in the ease with which it undergoes hydrolysis.

W. O. W.

**Preparation of Schiff's Bases from Nitroso-compounds.** A. K. PORAT-KOSCHITZ, Y. I. AUSCHKAP, and N. K. AMSLER (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 518—525).—In order to test the general applicability of the empirical rule laid down by Sachs (Abstr., 1900, i, 362; 1901, i, 272; 1902, i, 118, 119) to the effect that the methylene group is capable of reacting with the nitroso-group only when it is accompanied by strongly acidic groups, such as CN, NO<sub>2</sub>, CO·NH<sub>2</sub>, CHO, C·C, CO<sub>2</sub>H, etc., the authors have investigated the reactions occurring between nitroso-derivatives and 2-methylquinoline, 2:6-dimethylquinoline and 5-methylacridine, which are distinguished by the great mobility of the hydrogen atoms of their methyl groups, and condense, for example, with aldehydes with much greater ease than does 2:4-dinitrotoluene. With 2-methylquinoline and 2:6-dimethylquinoline no reaction occurs under the conditions employed by Sachs, and at a higher temperature or pressure the nitroso-amines are converted into nitroso-phenols, no reaction being observed with either the methyl- or dimethyl-quinoline.

But on boiling a mixture of 5-methylacridine with *p*-nitrosodiethylaniline in alcoholic solution with a small proportion of soda, condensation occurs in a manner analogous to that observed by Sachs. The product possesses all the properties of the azomethines, and, on decomposition with hydrochloric acid, gives 5-aldehydeacridine pure and in good yield.

When *p*-nitrosodiethylaniline is used in place of *p*-nitrosodimethylaniline, 5-methylacridine yields two products: (1) the azomethine compound (annexed formula): (2) a compound, C<sub>34</sub>H<sub>25</sub>ON<sub>3</sub>, forming orange-yellow needles, m. p. 210°.

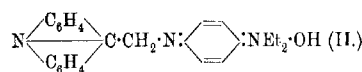
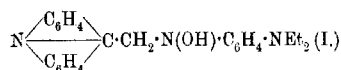
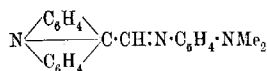
Assuming that this compound is formed by condensation of 5-methylacridine and *p*-nitrosodiethylaniline without

separation of water, that is, in the same manner as 5-methylacridine condenses with an aldehyde, it would have the structure (I); or, if the nitroso-compounds of amines and phenols be regarded as quinone-oximes and substituted

quinoneimides, it would be represented by (II).

The orange-yellow colour of the compound agrees better with the quinonoid formula (II) than with that (I) containing no chromophore-group, since the acridine series yields coloured compounds only on the introduction of auxochrome groups in the *p*-position to the central carbon atom. Attempts to remove the elements of water from this compound by means of various dehydrating agents were unsuccessful.

The conclusion is drawn that 5-methylacridine forms an exception to Sachs' rule.



4-Dimethylaminophenylazomethine-5-acridine (annexed formula), obtained from 5-methylacridine and *p*-nitrosodimethylaniline, forms dark red crystals, m. p. 231—232°.

4-Diethylaminophenylazomethine-5-acridine,  $C_{24}H_{23}N_3$ , forms dark red, almost black plates, m. p. 184°, and has the normal molecular weight in boiling benzene.

5-Aldehydroacridine (compare Beruthsen and Muhlert, Abstr., 1887, 849) crystallises in shining yellow needles, m. p. 145—146°. The hydrochloride, greenish-brown prisms, and the sulphate,

$(C_{14}H_9ON)_2 \cdot H_2SO_4$ ,  
small, yellowish-green needles, were prepared.

T. H. P.

Carbamide Derivatives of Phenylhydrazine. MAX BUSCH and OTTO LIMPACH (*Ber.*, 1911, 44, 1573—1583. Compare this vol. i, 334).

—Monothiodicarbamides of type (I)  $NHR \cdot CS \cdot NR \cdot NH \cdot CO \cdot NHR$  are readily obtained from  $\alpha$ -thiosemicarbazides,  $NHR \cdot CS \cdot NR \cdot NH_2$ , and carbimides, whilst the isomerides of type

(II)  $NHR \cdot CO \cdot NR \cdot NH \cdot CS \cdot NHR$

are prepared from  $\alpha$ -semicarbazides and isothiocarbamides, or, less easily, from  $\beta$ -thiosemicarbazides and carbimides. The two isomerides differ especially in that the thiocarbamyl residue is only very loosely bound to the  $\alpha$ -nitrogen atom of the hydrazine (type I), and is eliminated on fusion or on boiling with alcohol, whereas the  $\beta$ -thiocarbamide (type II) is completely stable. Phenylated derivatives of type (I) are not affected by boiling with alcoholic potassium hydroxide, but those of type (II) lose aniline and undergo a ring condensation to 1:4-diphenyl-

triazolone-3-thiol,  $NPh \cdot \begin{array}{c} C(SK) : N \\ \diagup \quad \diagdown \\ CO \quad NPh \end{array}$

Attempts to introduce a second thiocarbimide residue into  $\alpha$ -diphenylthiosemicarbazide gave  $\beta$ -diphenylthiosemicarbazide as the chief product. Addition of thiocarbimide to the  $\beta$  nitrogen first takes place, but at the same time the group attached to the  $\alpha$ -nitrogen is eliminated.

At higher temperatures phenylthiocarbimide reacts with  $\alpha$ - or  $\beta$ -diphenylthiosemicarbazides, liberating hydrogen sulphide, and forming phenylanilinothiodiazolone anil.

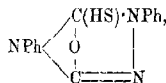
By the action of ethyl chlorocarbonylate on  $\alpha$ -diphenylthiosemicarbazide,  $\alpha$ -ethyl thiosemicarbazidecarboxylate (III),

$NHPh \cdot CS \cdot NPh \cdot NH \cdot CO_2Et$ ,

is obtained, together with the isomeride (IV),  $CO_2Et \cdot NPh \cdot NH \cdot CS \cdot NPh$ , which is also formed in quantity from  $\beta$ -diphenylthiosemicarbazide and ethyl chlorocarbonylate. Both esters are condensed by alcoholic potassium hydroxide to triazole derivatives. The former yields 5-thiol 1:4-diphenylendoxydihydrotriazole (V) (annexed formula) (compare Busch and Grohmann, Abstr., 1901, i, 616); the latter gives rise to 3-thiol-1:4-

diphenyltriazolone,  $NPh \cdot \begin{array}{c} C(SH) : N \\ \diagup \quad \diagdown \\ CO \quad NPh \end{array}$  (VI).

This triazole (V) is readily obtained directly





from ethyl phenylcarbazinate and phenylthiocarbimide in alcoholic potash. It is remarkable that some proportion of ethyl  $\beta$ -thiosemicarbazidecarboxylate (IV) is formed at the same time, and it is considered that in this reaction the carbethoxy-group wanders from the  $\beta$ - to the  $\alpha$ -nitrogen atom of the hydrazine. Such change could not be observed in ethyl  $\alpha$ -thiosemicarbazidecarboxylate under the influence of alcoholic potassium hydroxide.

$\alpha$ -Thiocarbanilido- $\beta$ -carbanilidophenylhydrazine,  
 $\text{NHPh}\cdot\text{CS}\cdot\text{NPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$ ,

crystallises in colourless needles, m. p.  $164^\circ$ . As directly prepared it contains traces of a sulphur-free substance separating in slender, colourless needles, m. p.  $214$ – $215^\circ$ , and also some 3-thiol-1:4-diphenyltriazolone, m. p.  $135^\circ$ , derived from the isomeric dicarbamide.

$\alpha$ -Carbanilido- $\beta$ -thiocarbanilidophenylhydrazine,  
 $\text{NHPh}\cdot\text{CO}\cdot\text{NPh}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$ ,

crystallises in slender, matted needles, m. p.  $178$ – $179^\circ$ .

$\alpha$ -Thiocarbanilido- $\beta$ -carbanilido-*o*-tolylhydrazine crystallises in colourless needles, m. p.  $181^\circ$ ; the corresponding *p*-tolylhydrazine compound has m. p.  $174^\circ$ . Neither substance contains any quantity of the  $\beta$ -isomeride.

Ethyl  $\beta\delta$ -diphenylthiosemicarbazide- $\alpha$ -carboxylate,  
 $\text{NHPh}\cdot\text{CS}\cdot\text{NPh}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ ,

from  $\alpha$ -diphenylthiosemicarbazide, has m. p.  $146^\circ$  (compare Busch and Grohmann, *loc. cit.*). The isomeric ethyl  $\alpha\delta$ -diphenylthiosemicarbazide- $\alpha$ -carboxylate from the  $\beta$ -isomeride separates in short leaflets, m. p.  $175$ – $176^\circ$ .  
 E. F. A.

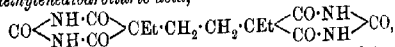
**Preparation of Dialkylethylenedibarbituric Acids.** ALBERT WOLFF (D.R.-P. 233968).—It is found that ethyl dialkylbutanetetra-carboxylates of the general formula  $\text{CR}(\text{CO}_2\text{Et})_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CR}(\text{CO}_2\text{Et})_2$  react under pressure with carbamide in the presence of alkali alcoholates.

The following compounds are described:

Ethyl dipropylbutanetetra-carboxylate, plates, m. p.  $103$ – $104^\circ$ .

Ethyl dibenzylbutanetetra-carboxylate, m. p.  $124$ – $125^\circ$ .

Diethylethylenedibarbituric acid,



colourless crystals, not melting below  $300^\circ$ , is prepared in 55% yield from ethyl diethylbutanetetra-carboxylate, carbamide, and sodium ethoxide.

Dipropylethylenedibarbituric acid has similar properties, and is obtained in 70% yield.  
 F. M. G. M.

**Quadriurates.** II. RUDOLF KOHLER (*Zeitsch. physiol. Chem.*, 1911, 72, 169–186. Compare this vol., i, 243).—A study of the solubility of uric acid in solutions of acid urates was based on the assumption that if quadriurates are formed, the solubility must be greater than in pure water, but smaller, on the other hand, if the quadriurates do not exist. Actually the solubility of uric acid decreases in presence of urates, the values agreeing with those

calculated when care is taken to prevent the absorption of carbon dioxide from the air. The conclusion is drawn that quadrurates are in reality mixtures of uric acid and acid urate.

E. F. A.

**Oxidation of 3- and 7-Methyluric Acids in the Presence of Ammonia.** OSKAR GROHMANN (*Annalen*, 1911, 382, 62—81. Compare Denicke, *Abstr.*, 1906, i, 938).—The two methyl acids have been oxidised by potassium ferricyanide in the presence of concentrated ammonium hydroxide. By using 1 atom of oxygen for each molecule of acid, it was not found possible to isolate compounds corresponding with iminoallantoin; as a rule, a portion of the acid was unacted on, and another portion more completely oxidised. From 7-methyluric acid a small amount of  $\beta$ -methylallantoin was obtained, but the same product is formed in the absence of ammonia. The compound,  $C_5H_{12}O_5N_6$ , is formed from the two acids when  $1\frac{1}{2}$  or 2 atoms of oxygen are used:  $C_5H_6O_3N_4 + 2NH_3 + 2O = C_5H_{12}O_5N_6 + CO_2$ . In addition a number of other products are formed, but these appear to be mainly decomposition products of the compound  $C_5H_{12}O_5N_6$ , which is presumably a methyl derivative of Denicke's compound,  $C_4H_{10}O_3N_5$ , and is to be represented as

and is to be represented as  $CO \begin{matrix} \text{NMe} \cdot C(NH_2) \cdot NH \cdot CO \cdot NH_2 \\ \text{NH} - C(OH) \cdot NH_2 \end{matrix}$   
or  $CO \begin{matrix} \text{NH} - C(NH_2) \cdot NH \cdot CO \cdot NH_2 \\ \text{NMe} \cdot C(OH) \cdot NH_2 \end{matrix}$ . It crystallises from warm water

in glistening, six-sided prisms, decomposing at  $185-187^\circ$ . It does not give the murexide reaction, and is transformed into resinous substances by concentrated mineral acids. When boiled with water for some time, ammonia is evolved, and carbamide, an amorphous substance, and an ammonium salt,  $C_5H_{13}O_5N_5$ , are formed. The amorphous substance, when crystallised from water, yields ammonium oxalate. The ammonium salt,  $C_5H_{13}O_5N_5$ , crystallises from dilute alcohol in monoclinic, six-sided prisms, decomposing at  $180-182^\circ$ . The corresponding silver salt crystallises from water in glistening plates, decomposing at  $204^\circ$  after turning dark-coloured at  $190^\circ$ . Treatment of the ammonium salt with hydrochloric acid yields methylloxaluric acid (Breusing, *Annalen*, 1902, 323, 167), carbamide, and ammonium chloride:

$C_5H_{13}O_5N_5 + HCl \rightarrow C_4H_6O_4N_2 + CON_2H_4 + NH_4Cl$ ,  
and attempts to synthesise the ammonium salt from oxaluric acid, carbamide, and ammonia were unsuccessful.

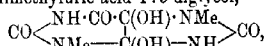
The compound  $C_5H_{12}O_5N_6$ , when warmed for fifteen minutes on the water-bath with 10% hydrochloric acid, yields methylparabanic acid, carbamide, and ammonium chloride:  $C_5H_{12}O_5N_6 + H_2O + 2HCl \rightarrow C_5H_4O_3N_5 + CON_2H_4 + NH_4Cl$ , and when boiled with dilute potassium hydroxide solution the compound is completely decomposed into ammonia and oxalic acid. When, however, the compound is warmed with 2*N* potassium hydroxide solution until dissolved, and then cooled and neutralised with 10% sulphuric acid, a compound,  $C_5H_{10}O_3N_4$ , decomposing at  $185-190^\circ$ , is obtained in the form of slender, felted needles.

In one experiment on the oxidation of the 7-methyl acid, a sparingly

soluble sodium salt,  $C_8H_6O_6N_2Na_2$ , was obtained from the mother liquor on the addition of sodium hydroxide.

The 3-methyl acid yields a stiff jelly with ammonium hydroxide solution, and its oxidation is most readily effected by adding a suspension of the acid in potassium ferrocyanide solution to concentrated ammonium hydroxide kept at  $0^\circ$ .  
J. J. S.

**Caffolide Degradation of 3:7-Dimethyluric Acid and of Theobromine.** HEINRICH BILTZ and ERNST TOPP (*Ber.*, 1911, 44, 1524—1532).—By the oxidation of theobromine by potassium chlorate and dilute hydrochloric acid at  $40$ — $50^\circ$ , Clemm obtained "hydroxy-3:7-dimethyluric acid," which is converted into a more soluble isomeride by warm water (*Abstr.*, 1898, i, 539). The former is now shown to be 3:7-dimethyluric acid 4:5-diglycol,



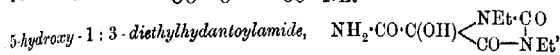
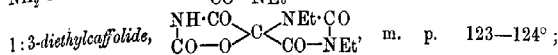
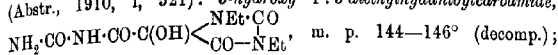
and the more soluble isomeride to be 5-hydroxy-1:9-dimethylhydantoyl carbamide,  $\text{NHMe} \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}(\text{OH}) \cdot \text{NMe} \cdot \text{CO}$  by their degrada-

tion successively into 1-methylcaffolide and 5-hydroxy-1-methylhydantoylamide. Since 3:7-dimethyluric acid 4:5-diglycol can be obtained from 8-chlorotheobromine, which itself is prepared by the chlorination of 3:7-dimethyluric acid, the preceding degradation is the third example of the complete caffolide degradation of a uric acid (compare *Abstr.*, 1910, i, 521; following abstract).

3:7-Dimethyluric acid 4:5-diglycol is obtained in 50—70% yield (as against Clemm's 10%) by passing a very rapid current of chlorine through a mixture of theobromine (not more than 10 grams) and glacial acetic acid containing rather more than the theoretical amount of water, the temperature being kept at about  $40^\circ$ . 8-Chlorotheobromine, which is conveniently obtained by rapidly chlorinating a suspension of theobromine in chloroform at the ordinary temperature, is also converted by the same treatment into 3:7-dimethyluric acid 4:5-diglycol, 8-chlorotheobromine 4:5-dichloride probably being formed as an intermediate product. The conversion of 3:7-dimethyluric acid 4:5-diglycol into 5-hydroxy-1:9-dimethylhydantoyl carbamide is simply effected by evaporating its aqueous solution on the water-bath. A mixture of the carbamide and ethyl acetate is saturated with hydrogen chloride at  $0^\circ$ , whereby methylamino hydrochloride and 1-methylcaffolide,  $\begin{array}{c} \text{NH} \cdot \text{CO} \diagup \text{C} \diagdown \text{NMe} \cdot \text{CO} \\ \text{CO} \text{---} \text{O} \quad \quad \quad \text{CO} \text{---} \text{NH} \end{array}$ , m. p. 218—219°

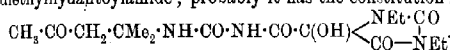
(decomp.), are obtained. The latter, which can be converted through its silver derivatives into allocaffeine (1:3:7-trimethylcaffolide, *Abstr.*, 1910, i, 522), is decomposed by boiling water into carbon dioxide and 5-hydroxy-1-methylhydantoylamide,  $\text{NH}_2 \cdot \text{CO} \cdot \text{C}(\text{OH}) \cdot \text{NMe} \cdot \text{CO}$ , m. p. 203—205° (decomp.), which is oxidised by potassium dichromate and boiling dilute sulphuric acid to methylparabanic acid. C. S.

**Caffolide Degradation of 7:9-Diethyluric Acid 4:5-Diglycol.**  
 HEINRICH BILTZ and ERNST TOPF (*Ber.*, 1911, 44, 1511—1523).—  
 7:9-Diethyluric acid 4:5-diglycol has been converted successively  
 into the following substances by reactions similar in the main to  
 those recorded in the case of 7:9-dimethyluric acid 4:5-diglycol  
 (Abstr., 1910, i, 521): 5-hydroxy-1:3-diethylhydantoylcarbamide,



m. p. 180—182°. The last compound forms an *O*-acetyl derivative,  
 m. p. 157—159°, an *O*-ethyl ether, m. p. 128—129° (which is  
 obtained better from 5-hydroxy-1:3-diethylhydantoylcarbamide and  
 alcoholic hydrogen chloride), and an *O*-methyl ether, m. p. 115—117°,  
 and is hydrolysed by aqueous barium hydroxide on the water-bath,  
 yielding ammonia, mesoxalic acid, and *s*-diethylcarbamide; it is  
 remarkably stable to oxidising agents, being unattacked by potassium  
 dichromate and sulphuric acid, except after heating on the water-bath  
 for five hours, whereby diethylparabanic acid is produced. Hydroxy-  
 diethylhydantoylamide is also unchanged by 3% or 10% hydrogen  
 peroxide and aqueous ammonia, but, after being kept for four weeks  
 with 30% hydrogen peroxide and a little ammonia, is converted into  
 diethylloxamide.

5-Hydroxy-1:3-diethylhydantoylcarbamide reacts with warm  
 acetone to form a substance,  $(\text{C}_{15}\text{H}_{24}\text{O}_6\text{N}_4)_2$ , m. p. 127—128° (decomp.),  
 which yields an odour of diacetoneamine with sodium hydroxide, does  
 not lose ammonia by treatment with hydrogen chloride, and is  
 oxidised by potassium dichromate and sulphuric acid to 5-hydroxy-  
 1:3-diethylhydantoylamide; probably it has the constitution:



The silver derivative of 1:3-diethylcaffolide is converted by ethyl  
 iodide into 1:3:7-triethylcaffolide,  $\text{C}_{11}\text{H}_{15}\text{O}_3\text{N}_3$ , b. p. 155°/15 mm.,  
 which has not been obtained pure.

At 200° 1:3-diethylcaffolide loses carbon dioxide (1 mol.), and is  
 converted into the lactamide of 5-hydroxy-1:3-diethylhydantoin-5-  
 carboxylic acid,  $\begin{matrix} \text{NH} \\ \diagup \\ \text{CO} \end{matrix} \text{C} \begin{matrix} \text{NEt}\cdot\text{CO} \\ \diagup \\ \text{CO}-\text{NEt} \end{matrix}$ , m. p. 280—290° (decomp.); the  
 lactamide from 1:3-dimethylcaffolide (*loc. cit.*) is constituted similarly.

C. S.

**Preparation and Phototropy of Certain Osazones. II.**  
 MAURICE PADOA and L. SANTI (*Atti R. Accad. Lincei*, 1911, [v], 20, i,  
 675—680. Compare Abstr., 1910, i, 779).— $\beta$ -Benzil-*m*-tolyllosazone,  
 $\text{C}_6\text{F}_5(\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_2$ , forms canary-yellow needles, m. p. 163°, and  
 is feebly phototropic.

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$\beta$ -Piperil-m-tolyllosazone,  $\text{CH}_3\cdot\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{C}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ , forms dark yellow needles, m. p.  $187^\circ$ , and is phototropic.

$\beta$ -Anisil-m-tolyllosazone,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ , crystallises in pale yellow scales, m. p.  $150\cdot5^\circ$ , and is phototropic.

$\beta$ -Piperil- $\beta$ -naphthylhydrazone,  $\text{CH}_3\cdot\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{C}(\text{C}_6\text{H}_5\cdot\text{O}_2\cdot\text{CH}_3)\cdot\text{N}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$ , forms a yellow, crystalline powder, m. p.  $162^\circ$ , and becomes darker on exposure to sunlight, but it cannot be stated with certainty that this is a phototropic change, since there is no apparent retrocession in the dark.

$\beta$ -Piperil- $\beta$ -naphthyllosazone (*loc. cit.*) forms an *additive* compound with chloroform,  $\text{C}_{36}\text{H}_{26}\text{O}_4\text{N}_4\cdot\text{CHCl}_3$ , which is obtained in yellow crystals, m. p.  $80^\circ$  (decomp.), and is non-phototropic.

$\beta$ -Anisil- $\beta$ -naphthyllosazone,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$ , forms stellar aggregates of pale yellow needles, m. p.  $165$ — $169^\circ$ , and exhibits phototropy. It forms a non-phototropic *additive* compound with benzene (1 mol.), in white needles, m. p.  $155$ — $158^\circ$ .

$\beta$ -Anisil-o-tolyllosazone forms non-phototropic, dark orange-yellow crystals, m. p.  $168^\circ$ .

$\beta$ -Anisil-p-tolyllosazone forms a pale yellow, phototropic powder, m. p.  $153^\circ$ , and gives a non-phototropic *additive* compound with benzene (1 mol.), m. p.  $166^\circ$ . T. H. P.

*o*-o'-Azoxybenzaldehyde. EUGEN BAMBERGER (*Ber.*, 1911, 44, 1966—1979).—The diethyl acetal of *o*-o'-azoxybenzaldehyde,

$\text{ON}_2[\text{C}_6\text{H}_4\cdot\text{CH}(\text{OEt})_2]_2$ , prepared by the reduction of *o*-nitrobenzaldehydediethylacetal (*p*-nitro- $\omega$ -diethoxytoluene) with methyl alcoholic sodium methoxide, crystallises in colourless prisms, m. p.  $76\cdot5^\circ$ . On hydrolysis with dilute hydrochloric acid in acetic acid solution, it yields *o*-o'-azoxybenzaldehyde.

*o*-o'-Azoxybenzaldehydedimethylacetal,  $\text{C}_{18}\text{H}_{22}\text{O}_5\text{N}_2$ , prepared in a similar manner to the ethyl derivative, crystallises in colourless plates, m. p.  $58\cdot5$ — $59\cdot5^\circ$ .

When heated with aqueous sodium hydroxide, *o*-o'-azoxybenzaldehyde yields 3-hydroxy-*o*-indazylbenzoic acid. Owing to the transformation into the lactone, this has a variable m. p., depending on the method of heating. When immersed in a bath at  $270^\circ$ , it partly melts, then solidifies, and finally melts again at  $299$ — $300^\circ$  (compare Carré, *Abstr.*, 1906, i, 705). It yields a crystalline *hydrochloride*, which is readily hydrolysed by water. When distilled over hot zinc dust and calcium carbonate, it gives aniline and phenazine. When oxidised with chromium trioxide in glacial acetic acid solution, it yields *o*-o'-azobenzoic acid, and, when warmed with glacial acetic acid or mineral acids, it is converted into the corresponding lactone.

*o*-o'-Azoxybenzaldehyde, on treatment with warm glacial acetic acid, yields 3-hydroxy-*o*-indazylbenzoic acid and its lactone, together with

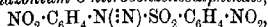
*o*-indazylbenzoic acid,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \diagup \text{CH} \diagdown \end{smallmatrix} \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ . The latter compound, which has also been prepared by reducing Pawlewski's *N*-*o*-nitrobenzylanthranilic acid (Abstr., 1904, i, 316) with hydrochloric acid and tin in boiling alcoholic solution, crystallises in lustrous, colourless leaves, m. p. 207.5—208.5°.

The transformation of *o*-*o*'-azoxybenzaldehyde into 3-hydroxy-*o*-indazylbenzoic acid and its lactone is also effected by exposure to light.

F. B.

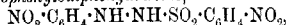
**Diazonium Sulphinates.** MAX CLAASZ (*Ber.*, 1911, 44, 1415—1419).—Previous attempts to prepare diazonium sulphinates by von Pechmann and Hantzsch have proved unsuccessful, but it is shown that such compounds can be prepared if the sulphinic acid contains negative substituents.

*o*-Nitrobenzenediazonium *o*-nitrobenzenesulphinate,

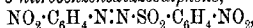


prepared by adding a diazotised solution of *o*-nitroaniline to an aqueous solution of sodium *o*-nitrobenzenesulphinate (this vol., i, 437), forms yellow crystals, and has most of the properties characteristic of diazonium salts. It explodes at about 100°, and when boiled with water yields *di*-*o*-nitrobenzenesulphone,  $\text{SO}_2(\text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$ , m. p. 164°. In alcoholic solution the sulphinate has  $\mu_{1000}^{18} = 1.538$ .

Sulphur dioxide reacts with a diazotised solution of *o*-nitroaniline, yielding *di*-*o*-nitrophenylsulphohydrazide,



which crystallises from ethyl alcohol in glistening, brown plates, decomposing at 153—155°. Its solutions in alkalis have a blood-red colour, and it reduces hot Fehling's solution. The same product can be obtained by condensing *o*-nitrophenylhydrazine with *o*-nitrobenzenesulphonyl chloride in alcoholic solution. When alkali is used, the products are potassium *o*-nitrobenzenesulphonate and azimidole. When oxidised with lead peroxide in the presence of acetone, the hydrazide yields *di*-*o*-nitrobenzenediazosulphone,



a compound isomeric with the diazonium sulphinate. It crystallises from glacial acetic acid in yellow, flocculent masses, decomposing at 145°, is not explosive, and does not couple with  $\beta$ -naphthol.

J. J. S.

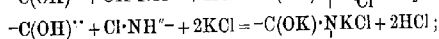
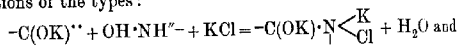
**Theory of the Action of Inorganic Salts on Proteins in Solution.** T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1911, 9, 303—326).—The author discusses the general questions of the precipitation and coagulation of proteins. The latter term is used when a large quantity of precipitating agent is required, and it takes place even when the protein is in the non-ionic state. The precipitating agent may or may not undergo decomposition during the process.

It is suggested that the high acid and alkali combining capacities of the proteins are not to be attributed to terminal amino- and carboxylic groups, but rather to the  $-\text{CO} \cdot \text{NH}-$  or  $-\text{C}(\text{OH}) \cdot \text{N}-$  groups present. In the latter form the group can react with acid in the following manner:

$-\text{C}(\text{OH})\cdot\text{N}^- + \text{H}^+ + \text{Cl}^- = -\text{C}(\text{OH})^+ + \text{Cl}^- \text{H} \text{N}^-$ , and with alkali as follows:  $-\text{C}(\text{OH})\cdot\text{N}^- + \text{Na}^+ + \text{OH}^- = -\text{C}(\text{ONa})^+ + \text{HO} \text{H} \text{N}^-$ , and in

each case only protein ions are formed. The following arguments are brought forward. (1) The compounds of proteins with acids and alkalis are excellent conductors in aqueous solution, and yet do not yield the ordinary ionic reactions, for example, a compound with hydrochloric acid does not yield chloride ions, and the equivalent conductivities at infinite dilution point to the presence of bulky organic ions. (2) Edestin is capable of displacing sodium hydroxide from its combination with hydrochloric acid, and casein can displace carbonic acid from its combination with calcium hydroxide, and yet edestin is not a strong base. The compounds do not undergo hydrolysis when diluted, and this is attributed to the fact that water does not enter into the equations given above (compare also Abstr., 1910, ii, 679). (3) Each equivalent of a mono-acid base neutralised by casein or serum-globulin yields two equivalents of protein salt, whereas if the neutralisation were effected by means of a carboxyl group each equivalent of the base would produce an equivalent of salt. (4) The osmotic pressure and depression of freezing point of casein increase in geometrical and not in arithmetical proportion on the addition of one, two, and three equivalents of a base. (5) According to Vernon (Abstr., 1904, ii, 626) the non-hydrolysed protein has nearly the same combining capacity for acid or alkali as the sum of its hydrolytic products.

It is suggested that the action of salts on the compounds of proteins with acids and alkalis is a dehydrating process, and various experiments in support of this suggestion are cited. The process of precipitation (as distinguished from coagulation) is represented by means of equations of the types:



the product  $-\text{C}(\text{OK}) \cdot \text{N} \text{KCl}$  tends to undergo hydrolysis in the presence of water, yielding  $-\text{C}(\text{OK}) \cdot \text{N} \text{HCl}$ , which is very sparingly soluble, and the formation of this results in precipitation. In the presence of a greater concentration of salt or of some other dehydrating agent, the hydrolysis is stopped, and hence no precipitation occurs. In the presence of still further amounts of dehydrating agents or on heating, the terminal amino- and carboxyl groups of the protein molecules react, yielding water and anhydrides which are usually insoluble, and thus coagulation is brought about.

J. J. S.

**Sulphur in Proteins. Thiopolypeptides.** TREAT B. JOHNSON and GERALD BURNHAM (*J. Biol. Chem.*, 1911, 9, 331—332).—It is suggested that the sulphur present in proteins may be present in groups similar to those in which the oxygen is usually found, namely,  $-\text{SH}$  and  $-\text{CS}-\text{NH}-$ . Cystein represents a compound containing the thiol group, but hitherto compounds with the  $-\text{CS}-\text{NH}-$  group have

not been isolated. Several compounds of this type and their derivatives have been prepared, and are being investigated. J. J. S.

**The Isoelectric Point of Genuine and Denaturated Serum-Albumin.** LEONOR MICHAELIS and HEINRICH DAVIDSOHN (*Biochem. Zeitsch.*, 1911, 33, 456—473).—The authors employed with small modifications the methods already described, and found that the coagulation optimum point for denaturated albumin was  $0.4 \times 10^{-5}$ . The same isoelectric point was found by the method of electrocataphoresis. The isoelectric point for genuine albumin found by the latter method was  $2 \times 10^{-5}$ . The electrolyte content of the mixture (which varied between  $N/10$ - and  $N/50$ -sodium acetate) had no appreciable influence. From these results it was found that the relative acidity,  $k_a/k_b$ , of albumin falls during denaturation from  $7 \cdot 10^4$  to  $3 \cdot 10^3$ . S. B. S.

**Hydrolysis of Sodium "Iodeigon."** ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1911, 72, 374—379. Compare Mosse and Neuberg, *Abstr.*, 1903, ii, 496).—When sodium "iodeigon" is boiled with barium hydroxide solution, 96.5% of the iodine is eliminated as hydriodic acid within the first 4.5 hours. Non-crystallisable resins are also obtained, but no indication of di-iodotyrosine and no o-iodobenzoic acid. The behaviour of "iodeigon" towards hydrolysing agents is thus different from that of iodo-albacid (this vol., i, 203) and iodo-gludin (*ibid.*, 372). J. J. S.

**Analysis of the Products of Hydrolysis of Wheat Gliadin.** THOMAS B. OSBORNE and H. H. GUEST (*J. Biol. Chem.*, 1911, 9, 425—438).—Owing to improved methods, it appeared desirable to undertake a fresh investigation of gliadin, a protein much used in nutrition experiments. Analytical results are given in full, in reference to the partition of nitrogen, the yield of amino-acids, and these results are compared with those in other proteins. The total yield of amino-acids amounted to 83.54% of the original protein, and the deficit is probably due to losses incurred in estimating those amino-acids which are obtained from their esters. W. D. H.

**A New Decomposition Product of Keratin which gives Millon's Reaction.** ROSS A. GORTNER (*J. Biol. Chem.*, 1911, 9, 355—357).—A positive reaction with Millon's reagent in a protein is generally taken as evidence of the presence of tyrosine. It is, however, shown that in a melano-protein prepared from black wool after hydrolysis yielded, not only tyrosine, but there was in the mother liquor a substance which still gave Millon's reaction with great intensity. This substance is evidently an aromatic phenolic material, but it has not yet been identified. W. D. H.

**The Laws of Enzyme Action.** P. VON GRÜTZNER [with W. WALDSCHMIDT] (*Pflüger's Archiv*, 1911, 141, 63—117).—Experiments showed that, under similar conditions, the amount of protein or gelatin digested is in direct linear proportion to the quantity of enzyme present. This applies to experiments with pepsin, trypsin, and ptyalin when the time occupied is short; if prolonged, this law no



longer holds, but the rate of change conforms to Schütz' law, and this finally ceases to apply. The retardation of change is greater in the case of high concentration of enzyme.

When equal amounts of change are allowed to take place, the velocity of change is in direct proportion to the amount of enzyme. If the substrate be increased, there ensues in the case of pepsin (less in the case of ptyalin) a reduction in the rate of change. On the other hand, under similar conditions, the higher concentrations of trypsin digest at a proportionately greater rate than the lower concentrations.

The view is expressed that no single law can be applied to the whole course of enzymic change.

H. B. H.

**The Digestibility of White of Egg as Influenced by the Temperature at which it is Coagulated.** PHILIP FRANK (*J. Biol. Chem.*, 1911, 9, 463—470).—The Mett tube method is regarded as untrustworthy, owing to the inclusion of air bubbles, the setting of the albumin in the tubes in uneven layers, and to the fact that the digestibility of the egg-white varies according to the temperature used in producing coagulation. The last factor is regarded as very important and is treated at length.

W. D. H.

**The Identity of Pepsin and Rennet.** AGNES ELLEN PORTER (*J. Physiol.*, 1911, 42, 389—401).—Several commercial preparations of rennet were found to be milk curdling, but non-peptic, or were antipeptic. The antipeptic material is indifferent to rennet, and can be removed by dialysis. A rennet zymoid occurred spontaneously, which was indifferent to pepsin. The results are in favour of the view that the two enzymes are not identical.

W. D. H.

**Nucleases.** II. PROBUS A. LEVENE and FLORENTIN MEDIGREANU (*J. Biol. Chem.*, 1911, 9, 389—402).—That the final oxidation, etc., of purine bases is due to the graded action of specific enzymes has been established by Walter Jones and Schittenhelm, and is confirmed by the present experiments. The so-called nucleases really include three groups of enzymes. These may be designated: (1) *Nucleinases*, which resolve the molecule into mono-nucleotides; such an enzyme occurs in all organs, and in pancreatic juice, but not in gastric juice. (2) *Nucleotidases*, which liberate phosphoric acid, leaving the carbohydrate base complexes (nucleosides) intact. They are present in all organs, juices, and in intestinal juice, but are absent from gastric and pancreatic juices. There are probably specific enzymes to deal with each nucleotide. (3) *Nucleosidases* are the enzymes which cleave hydrolytically the nucleosides into their components, the carbohydrate ribose, and their bases of the purine or pyrimidine groups. These are absent in all the digestive juices and in the plasma of the pancreas, but are present in the plasmata of most other organs.

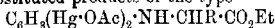
W. D. H.

**The Inhibition of the Action of Invertase.** ANSLEM ERIKSSON (*Zeitsch. physiol. Chem.*, 1911, 72, 313—338).—Invertase can be removed wholly or in part from its solutions by charcoal. The removal, and in this way the inhibition, of its action is greater if

the charcoal is added before the mixing of the enzyme and substrate than if it is added after the mixture has occurred. Time and temperature are other factors. Normal serum also inhibits the activity of invertase, and the order in which it is added is a factor, although not so great a one, as in the case of charcoal. Inhibiting substances occur also in the invertase solution itself; they are not destroyed by boiling, they diffuse very slowly through a membrane, and are not to any great extent absorbed by charcoal.

W. D. H.

**Synthesis of Mercuriated  $\alpha$ -Anilino-fatty Acids.** WALTER SCHOELLER, WALTHER SCHRAUTH, and PAUL GOLDACKER (*Ber.*, 1911, 44, 1300—1312). In order to determine the influence exerted by the amino-group on the introduction of mercury into the benzene nucleus, the authors have investigated the action of mercuric acetate on the ethyl esters of  $\alpha$ -anilinoacetic acid and its homologues. It is found that the introduction of mercury proceeds more easily as the series is ascended. Whilst ethyl  $\alpha$ -anilinoacetate forms only a mono-substitution product, the propionic ester reacts with mercuric acetate in equal molecular proportions, yielding a mixture of the mono- and di-substitution products. In the case of the butyric and isovaleric esters, only disubstituted products of the type



could be obtained.

*Ethyl o-acetoxymercurianilinoacetate*,  $\text{OAc}\cdot\text{Hg}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , prepared by the addition of aqueous mercuric acetate to a methyl alcoholic solution of ethyl anilinoacetate, forms small, tabular crystals, m. p.  $132^\circ$  (corr.), with previous softening at  $129^\circ$  (corr.). When shaken with bromine in aqueous potassium bromide, it yields *ethyl o-bromoanilinoacetate*, which crystallises in white needles, m. p.  $82$ — $83^\circ$ ; the corresponding *o-iodo*-compound forms greyish-white leaflets, m. p.  $86$ — $87^\circ$ .

*Ethyl o-chloromercurianilinoacetate*,  $\text{HgCl}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , is obtained by the action of sodium chloride on the preceding acetoxymercuri-ester in aqueous alcoholic solution; it crystallises in needles or rhombic plates, m. p.  $152.5^\circ$  (corr.), with previous sintering at  $150.5^\circ$  (corr.). *Ethyl o-bromomercurianilinoacetate* forms rhombic plates, which sinter at  $144^\circ$ , and have m. p.  $147.5^\circ$  (corr.); the corresponding *iodo*-ester crystallises in lustrous leaflets, m. p.  $139$ — $140^\circ$  (corr.), with previous sintering at  $137$ — $138^\circ$  (corr.).

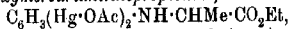
*o-Hydroxymercurianilinoacetic anhydride*,  $\text{C}_6\text{H}_4\begin{matrix} \text{NH}-\text{CH}_2 \\ \diagup \text{Hg}\cdot\text{O}\cdot\text{CO} \end{matrix}$ , pre-

pared by hydrolysing the acetoxymercuri-ester with sodium hydroxide and acidifying the resulting solution, decomposes at  $228^\circ$  (corr.); the copper salt,  $(\text{HO}\cdot\text{Hg}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2)_2\text{Cu}$ , decomposes at  $193$ — $197^\circ$  (corr.); the lead, iron, calcium, silver, mercury, and platinum salts are also mentioned.

*Ethyl o-acetoxymercurianilinoacetonpropionate* is obtained together with a small quantity of the diacetoxymercuri-ester by the reaction of equal molecular quantities of mercuric acetate and ethyl  $\alpha$ -anilinoacetonpropionate, but since it could not be obtained free from the accompanying di-mercuri-ester, it was converted by the action of sodium chloride into

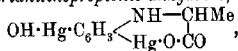
*ethyl a-chloromercurianilinopropionate*,  $\text{HgCl} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$ ; this crystallises in microscopic needles, m. p.  $165.5^\circ$  (corr.).

*Ethyl a-diacetoxymercurianilinopropionate*,



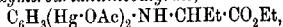
which crystallises in leaflets, m. p.  $186^\circ$  (corr.), is prepared by the interaction of mercuric acetate (2 mols.) and ethyl a-anilino-propionate (1 mol.) in aqueous methyl-alcoholic solution; a less soluble, apparently polymeric form, is produced simultaneously. When treated with sodium chloride, it yields *ethyl a-dichloromercurianilinopropionate*,  $\text{C}_{11}\text{H}_{13}\text{O}_2\text{NCl}_2\text{Hg}_2$ , which forms small needles, m. p.  $131^\circ$  (corr.), with previous softening at  $128^\circ$ ; the corresponding *dibromomercuri-ester* crystallises in needles, m. p.  $128.5^\circ$  (corr.), with previous softening.

*a-Dihydroxymercurianilinopropionic anhydride*,



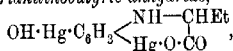
prepared from the diacetoxymercuri-ester by hydrolysis with aqueous sodium hydroxide, decomposes at  $223^\circ$  (corr.).

*Ethyl a-diacetoxymercurianilinobutyrate*,



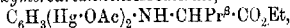
prepared from ethyl a-anilinobutyrate in the usual manner, crystallises in stout rods, sintering at  $150^\circ$ , m. p.  $154.5^\circ$  (corr.). On treatment with sodium chloride, it yields *ethyl a-dichloromercurianilinobutyrate*,  $\text{C}_{12}\text{H}_{15}\text{O}_2\text{NCl}_2\text{Hg}_2$ , which forms slender needles, m. p.  $127^\circ$  (corr.), with previous softening at  $125^\circ$  (corr.); the corresponding *dibromomercuri-ester* crystallises in needles, softening at  $125^\circ$  (corr.), m. p.  $127^\circ$  (corr.); the *di-iodo-ester* has m. p.  $120^\circ$  (corr.).

*a-Dihydroxymercurianilinobutyric anhydride*,



is obtained by hydrolysing the preceding diacetoxymercuri-ester; when heated, it becomes yellowish-brown at  $200^\circ$ , and decomposes at  $208^\circ$  (corr.); it readily takes up water on exposure to air, forming  $\text{C}_{10}\text{H}_{13}\text{O}_4\text{NHg}$ .

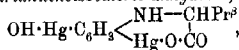
*Ethyl a-diacetoxymercurianilinoisovalerate*,



prepare from ethyl a-anilinoisovalerate and mercuric acetate, crystallises in tufts or stellar aggregates of needles, m. p.  $126^\circ$  (corr.).

*Ethyl a-dichloromercurianilinoisovalerate*,  $\text{C}_{13}\text{H}_{17}\text{O}_2\text{NCl}_2\text{Hg}_2$ , forms microscopic rods, m. p.  $122^\circ$  (corr.); the corresponding *dibromomercuri-ester* occurs in two forms: a granular, sandy, amorphous modification, which decomposes at  $215^\circ$  without melting, and is insoluble in ethyl acetate; and a soluble form crystallising in tufts of white needles, m. p.  $135^\circ$  (corr.); the *di-iodomercuri-ester* forms yellow needles, m. p.  $129^\circ$  (corr.).

*a-Dihydroxymercurianilinoisovaleric anhydride*,



decomposes at  $226^\circ$  (corr.), and readily takes up water on exposure to air. F. B.

## Organic Chemistry.

The Grignard Reaction in its Application to Dihalogen Compounds. I. JULIUS VON BRAUN and WLADISLAUS SOBECKI (*Ber.*, 1911, 44, 1918—1931. Compare Abstr., 1907, i, 997; Zelinsky and Gutt, *ibid.*, 676; Grignard and Vignon, *ibid.*, 689).—The authors find that the interaction of magnesium with  $\alpha\delta$ -dibromobutane,  $\alpha\epsilon$ -dibromopentane,  $\alpha\eta$ -dibromoheptane, or  $\alpha\kappa$ -diiododecane yields only about half of the theoretical amount of the normal magnesium compound,  $\text{MgX} \cdot [\text{CH}_2]_n \cdot \text{MgX}$ , the remainder of the dihalogen derivative being converted into a mixture of magnesium compounds of the general formula  $\text{MgX} \cdot [\text{C}_n\text{H}_{2n}]_r \cdot \text{MgX}$ .

No evidence of the formation of cyclic or unsaturated hydrocarbons, or of magnesium compounds of the type  $\text{MgX} \cdot [\text{CH}_2]_n \cdot \text{Br}$ , was obtained.

The magnesium compound of  $\alpha\delta$ -dibromobutane reacts with carbon dioxide, yielding cyclopentanone, sebacic acid, and dodecamethylene-dicarboxylic acid.

When treated with water, the magnesium compound of  $\alpha\epsilon$ -dibromopentane gave pentane, decane, pentadecane, and eicosane, together with still higher homologues.

The magnesium compound of  $\alpha\eta$ -dibromoheptane, when similarly treated, yields a mixture of hydrocarbons, from which heptane and tetradecane were isolated; it reacts with carbon dioxide, yielding a mixture of acids,  $\text{CO}_2\text{H} \cdot [\text{CH}_2]_{7n} \cdot \text{CO}_2\text{H}$ , from which azelaic acid is separated by boiling it with water.

By decomposing the magnesium compound of  $\alpha\kappa$ -diiododecane with water, decane, eicosane and tetracontane were obtained; the action of carbon dioxide yields a mixture of the acids  $\text{CO}_2\text{H} \cdot [\text{CH}_2]_{10n} \cdot \text{CO}_2\text{H}$ , from which decane- $\alpha\kappa$ -dicarboxylic acid may be readily separated by extraction with hot water.

The magnesium compound of  $\alpha\epsilon$ -dibromopentane reacts with acetone, yielding the following compounds: (1)  $\beta$ -methylheptan- $\beta$ -ol (Muset, Abstr., 1907, i, 374), the formation of which takes place according to the scheme:  $\text{COMe}_2 + \text{MgBr} \cdot [\text{CH}_2]_5 \cdot \text{MgBr} \xrightarrow{\text{H}_2\text{O}} \text{MgBr} \cdot \text{O} \cdot \text{CMe}_2 \cdot [\text{CH}_2]_5 \cdot \text{MgBr} \rightarrow \text{OH} \cdot \text{CMe}_2 \cdot [\text{CH}_2]_5 \cdot \text{H}$ ; (2) a liquid,  $\text{C}_{11}\text{H}_{22}\text{O}$ , b. p. 107—109°/14 mm.,  $D_4^{20}$  0.8467,  $n_D^{20}$  1.45512, having an odour resembling citronellol, and consisting probably of a mixture of the unsaturated alcohols,  $\text{OH} \cdot \text{CMe}_2 \cdot [\text{CH}_2]_5 \cdot \text{CMe} \cdot \text{CH}_2$  and

$\text{OH} \cdot \text{CMe}_2 \cdot [\text{CH}_2]_4 \cdot \text{CH} \cdot \text{CMe}_2$ ;  
(3)  $\beta$ -dimethylnonan- $\beta$ -diol,  $\text{OH} \cdot \text{CMe}_2 \cdot [\text{CH}_2]_5 \cdot \text{CMe}_2 \cdot \text{OH}$ , which has b. p. 135—145°/12 mm., and readily solidifies to a white, crystalline mass, m. p. 77°.

$\beta$ -Dibromo- $\beta$ -dimethylnonane,  $\text{C}_{11}\text{H}_{22}\text{Br}_2$ , prepared by the action of hydrobromic acid on the preceding glycol in glacial acetic acid solution, is a viscid oil, which loses hydrogen bromide when heated with pyridine, and is converted into the unsaturated hydrocarbon,

$C_{11}H_{20}$ , b. p. 180—183°,  $D_4^{20} 0.7709$ ,  $n_D^{20} 1.4504$ ; the latter compound yields an oily *tetrabromide*, and probably consists of a mixture of two or three structural isomerides.

By the interaction of trioxymethylene with the magnesium compound of  $\alpha$ -dibromopentane, the authors hoped to find a ready means of passing from the pentamethylene group to the heptamethylene group:

$MgBr \cdot [CH_2]_5 \cdot MgBr + 2CH_2O \rightarrow OH \cdot CH_2 \cdot [CH_2]_5 \cdot CH_2 \cdot OH$   
 Their hopes were, however, not realised, partly on account of the difficulty with which trioxymethylene enters into reaction, and partly because of the difficulty of isolating the easily soluble heptane- $\alpha$ -glycol from the reaction product.  
 F. B.

**Attempted Preparation of Methylene Derivatives.** HERMANN STAUDINGER and OTTO KUPFER (*Ber.*, 1911, 44, 2194—2197).—The authors have attempted in various ways to decompose substances such as tetrachloroethylene, tetraphenylethylene, benzyl chloride, benzylidene chloride, chlorodiphenylmethane, and ethyl orthoformate, in the hope of obtaining compounds containing a bivalent carbon atom attached to two other elements or to two carbon atoms. In every case, however, the result is negative, the methylene derivative, if formed temporarily, being converted by polymerisation into an ethylene derivative or by additive reactions into a derivative of methane. C. S.

**Reduction and Oxidation by Catalysis.** PAUL SABATIER (*Ber.*, 1911, 44, 1984—2001).—A lecture before the German Chemical Society, summarising the author's experiments on the catalytic reduction of organic compounds by passing their vapours, mixed with hydrogen, through metallic tubes, especially nickel, at a temperature of about 180°. At 250° the same metals bring about a catalytic oxidation, for example, of alcohols to aldehydes or ketones.  
 E. F. A.

**Cyanopinacolin and Some Compounds Derived From It.** OSKAR WIDMAN and ERIK WAHLBERG (*Ber.*, 1911, 44, 2065—2071).—By the interaction of equivalent quantities of bromine and pinacolin, a mixture of bromo- and dibromo-pinacolin is obtained.

$\omega$ -Bromopinacolin is a colourless liquid, which attacks the skin and eyes, b. p. 77—78°/15 mm., 184—188°/760 mm.,  $D_4^{20} 1.33$ .

$\omega$ -Dibromopinacolin has m. p. 75° (compare Scholl and Weil, *Chem. Zeit.*, 1899, 23, 189).

The monobromide reacts with potassium cyanide, yielding  $\omega$ -cyanopinacolin (*tert.*-valerylacetonitrile); this forms colourless, well-shaped crystals with many faces, and centimetre-long prisms, m. p. 68—68.5°. The potassium salt,  $CMe_3 \cdot C(OK) \cdot CH \cdot CN$ , crystallises in colourless tablets.

The hydrochloride of *tert.*-valerylacetimino-ether,  
 $CMe_3 \cdot CO \cdot CH_2 \cdot C(OEt) \cdot NH \cdot HCl$ ,  
 prepared by the action of hydrogen chloride on cyanopinacolin dissolved in a mixture of alcohol and ether, crystallises in large four- or six-sided prisms, m. p. 126—127° (decomp.) when quickly heated, or

m. p. 131° (slowly heated). The *platinichloride* forms long, yellow needles, m. p. 135°.

tert. *Valerylacetamide*, obtained on heating the imino-ether hydrochloride, crystallises in large, glistening plates, m. p. 95°.

*Phthaliminopinacolin*, prepared by heating bromopinacolin with potassium phthalimide in alcohol, crystallises in lustrous, stout, four-sided prisms with hemihedric faces, m. p. 102°.

*Pinacolylphthalamic acid* crystallises in well formed four- or six-sided plates or prisms, m. p. 132°.

*Pinacolylamine*,  $\text{CMe}_2\text{CO}\cdot\text{CH}_2\cdot\text{NH}_2$ , is obtained as *hydrochloride* on evaporating the phthalamic acid with hydrochloric acid; it is deliquescent. The base was characterised by warming with potassium cyanate and conversion into 2-hydroxy-5-tert.-butylglyoxaline,

$\text{CMe}_2\text{C}\begin{array}{c} \diagup \text{CH-N} \\ \diagdown \text{NH}\cdot\text{C}\cdot\text{OH} \end{array}$  which separates in needles, m. p. 277—278°.

E. F. A.

**Effect of Heating Mixed Esters of Carbonic Acid.** ALFRED EINHORN and LEO ROTHLAUF (*Annalen*, 1911, 382, 237—265. Compare Einhorn, Abstr., 1909, i, 568).—The velocity with which mixed carbonic esters lose carbon dioxide and yield phenolic ethers depends largely on the nature of the alkyl group present. With common alkyl groups such as methyl and ethyl, the decomposition takes place slowly, but becomes more rapid when strongly basic substituents are present in the alkyl group. Attention is drawn to the fact that numerous isolated examples of this type of decomposition are recorded in chemical literature. The formation of esters of organic acids by the action of ethyl chlorocarbonate on sodium salts (R. and W. Otto, Abstr., 1888, 813; 1891, 288) is a reaction of a similar type; a mixed anhydride,  $\text{R}\cdot\text{CO}\cdot\text{O}\cdot\text{CO}\cdot\text{OEt}$ , is formed as an intermediate product, and decomposes into carbon dioxide and the ester. Similarly, the mixed anhydrides, formed by the action of the salts of aromatic acids on diphenylcarbamide chloride in the presence of pyridine, lose carbon dioxide and yield diphenylated acid amides (Herzog, Abstr., 1909, i, 568; Herzog and Hancu, 1908, i, 268). Acid anhydrides with catalysts yield ketones (Mailhe, Abstr., 1909, i, 692; compare Senderens, *ibid.*, 287), and by heating benzyl and *p*-nitrobenzyl esters of chlorocarbonic acid, benzyl chloride and *p*-nitrobenzyl chloride are formed (Thiele and Dent, Abstr., 1898, i, 15; compare also F. Hofmann, *Zeitsch. angew. Chem.*, 1908, 21, 1986). Similarly, aldehydes when heated with carbonyl chloride yield carbon dioxide and the corresponding chloride.

Guaiacyl methyl carbonate,  $\text{OMe}\cdot\text{C}_6\text{H}_3\cdot\text{O}\cdot\text{CO}\cdot\text{Me}$ , obtained by the action of methyl chlorocarbonate on guaiacol in the presence of pyridine, has b. p. 132—134°/16 mm., and when heated at 234° and then at 218° yields guaiacol and catechol dimethyl ether, together with guaiacyl carbonate and unaltered guaiacyl methyl carbonate. Guaiacyl ethyl carbonate has b. p. 265°, and when boiled for seven days in a reflux apparatus yields guaiacol and its ethyl ether.

Resorcinyl diethyl dicarbonate,  $\text{C}_6\text{H}_4(\text{O}\cdot\text{CO}_2\text{Et})_2$ , has b. p. 174—176°/19 mm. or 270—288° under atmospheric pressure (Wallach

gives 298—302°). When boiled for twenty-eight hours it yields resorcinol mono- and di-ethyl ethers, and an insoluble product, probably a high molecular resorcinylic carbonate. *Resorcinylic ethyl carbonate*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}_2\text{Et}$ , when freed from resorcinol by digesting with water, crystallises from light petroleum in plates, m. p. 52—53°, b. p. 170—173°/11 mm. or 274° under atmospheric pressure, and when boiled for seven hours yields resorcinol monoethyl ether, resorcinylic carbonate, and resorcinol. By boiling  $\beta$ -naphthyl methyl carbonate for 46.5 hours,  $\beta$ -naphthol, its carbonate, and methyl ethers are obtained. Aryl-diethylaminoethyl carbonates can be prepared by the action of diethylaminoethanol on phenyl chlorocarbonates (D.R.P. 118537) in benzene solution.

Guaiacyl chlorocarbonate (Barral and Morel, Abstr., 1899, i, 802) is best prepared by the action of a benzene solution of carbonyl chloride on guaiacol in the presence of quinoline, and with diethylaminoethanol yields guaiacyl diethylaminoethyl carbonate, the *hydrobromide* of which,  $\text{C}_{14}\text{H}_{21}\text{O}_4\text{N}\cdot\text{HBr}$ , crystallises from acetone in rhombohedra, m. p. 99—100°.

*Diethylaminoethylguaiacol*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_2\text{H}_4\cdot\text{NEt}_2$ , obtained by distilling guaiacyl diethylaminoethyl carbonate once or twice under reduced pressure, is a colourless oil, b. p. 148—150°/10 mm. The *hydrobromide* has m. p. 127—128°. *Thymyl diethylaminoethyl carbonate*,  $\text{C}_6\text{H}_2\text{MePr}^2\cdot\text{O}\cdot\text{CO}_2\cdot\text{C}_2\text{H}_4\cdot\text{NEt}_2$ , obtained from *thymyl chlorocarbonate*, b. p. 122—124°/25 mm., is a yellow oil; the *hydrobromide* crystallises from alcohol in slender needles, m. p. 160°, and the *citrate*,  $\text{C}_{22}\text{H}_{35}\text{O}_{10}\text{N}$ , in microscopic crystals, m. p. 90—95°. When distilled twice under reduced pressure, the base gives a quantitative yield of *diethylaminoethylthymol*,  $\text{C}_6\text{H}_2\text{MePr}^2\cdot\text{O}\cdot\text{C}_2\text{H}_4\cdot\text{NEt}_2$ , as a liquid with b. p. 126°/18 mm. The *citrate*,  $\text{C}_{22}\text{H}_{35}\text{O}_8\text{N}$ , crystallises from alcohol in prisms, m. p. 142—143°.

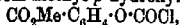
$\beta$ -Naphthyl chlorocarbonate,  $\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{COCl}$ , has b. p. 150—152°/9 mm., and crystallises from light petroleum in slender, yellow needles, m. p. 65—66°.  $\beta$ -Naphthyl diethylaminoethyl carbonate,

$\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{CO}_2\cdot\text{C}_2\text{H}_4\cdot\text{NEt}_2$ , is a basic oil; its *hydrochloride*,  $\text{C}_{17}\text{H}_{21}\text{O}_3\text{N}\cdot\text{HCl}$ , crystallises from acetone in colourless needles, m. p. 141°, and when the base is distilled twice under reduced pressure the *diethylaminoethyl ether* of  $\beta$ -naphthol,  $\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{C}_2\text{H}_4\cdot\text{NEt}_2$ , is obtained as a yellow oil, b. p. 202°/18 mm.; its *hydrochloride*,  $\text{C}_{16}\text{H}_{19}\text{ON}\cdot\text{HCl}$ , crystallises from a mixture of alcohol and ether in small plates, m. p. 138—139°. The *chlorocarbonate* derived from ethyl salicylate,  $\text{COCl}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ , is a colourless oil, b. p. 144°/12 mm., and reacts with diethylaminoethanol, yielding the *ethyl ester*,  $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}_2\cdot\text{C}_2\text{H}_4\cdot\text{NEt}_2$ , as a yellow oil, the *hydrobromide* of which forms minute crystals from acetone, m. p. 106—108°. *Ethyl diethylaminoethylsalicylate*,

$\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_2\text{H}_4\cdot\text{NEt}_2$ , has b. p. 179—180°/10 mm., and its *hydrochloride* crystallises from ethyl acetate in needles, m. p. 112°. The *methyl ester*,

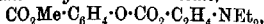
$\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}_2\cdot\text{C}_2\text{H}_4\cdot\text{NEt}_2$ , yields a *hydrobromide*, which crystallises from a mixture of acetone and ether in needles, m. p. 127—130°.

The chlorocarbonate from methyl *p*-hydroxybenzoate,



as b. p.  $144^\circ/13$  mm., and crystallises from light petroleum in yellow needles, m. p.  $58^\circ$ .

Methyl *p*-diethylaminoethylcarbonatobenzoate,



is a yellow oil; its hydrochloride crystallises from absolute alcohol as glistening needles, m. p.  $133$ — $134^\circ$  (decomp.), and decomposes in the presence of water, yielding carbon dioxide, diethylaminoethanol hydrochloride, and methyl-*p*-hydroxybenzoate.

Methyl *p*-diethylaminoethoxybenzoate,  $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_2\text{H}_5\cdot\text{NEt}_2$ , has b. p.  $186$ — $189^\circ/15$  mm.; its hydrochloride crystallises from ethyl acetate in thin, glistening plates, m. p.  $147^\circ$ .

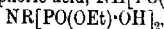
Ethyl diethylaminoethyl carbonate,  $\text{OEt}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_2\text{H}_5\cdot\text{NEt}_2$ , obtained from ethyl chlorocarbonate and diethylaminoethanol, is a colourless oil, b. p.  $91$ — $94^\circ/10$  mm.; the citrate,  $\text{C}_{15}\text{H}_{27}\text{O}_{10}\text{N}$ , crystallises from ethyl acetate in needles, m. p.  $93$ — $98^\circ$ . When the base is boiled in reflux apparatus, the temperature registered is  $207^\circ$ , but falls and finally remains constant at  $172^\circ$ , the products of decomposition being ethyl alcohol, ethyl carbonate, and diethylaminoethanol.

Menthyl diethylaminoethyl carbonate,  $\text{C}_{10}\text{H}_{19}\cdot\text{O}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_2\text{H}_5\cdot\text{NEt}_2$ , obtained from menthyl chlorocarbonate, b. p.  $105$ — $106^\circ/12$  mm., and diethylaminoethanol, is a colourless liquid, b. p.  $179$ — $180^\circ/9$  mm.; its hydrochloride,  $\text{C}_{17}\text{H}_{33}\text{O}_3\text{N}\cdot\text{HCl}$ , crystallises from ethyl acetate in prismatic needles, m. p.  $142^\circ$ . When the base is boiled for some hours, the temperature falls from  $215^\circ$  to  $204^\circ$ , and menthol, menthyl carbonate, m. p.  $105^\circ$ , diethylaminoethanol, and its carbonate are formed.

J. J. S.

## Esters and Amides of the Phosphoric Acids. II. Attempts

to Prepare Substances Allied to the Lecithins. KURT LANGFELD (*Ber.*, 1911, 44, 2076—2087. Compare Abstr., 1910, i, 536).—Esters of metaphosphoric acid unite with alcohols to form esters of orthophosphoric acid of the type  $\text{OR}\cdot\text{PO}(\text{OR}')\cdot\text{OH}$ . At the ordinary temperature the addition of alcohol takes place quantitatively in the course of four to five days, but in the case of solid alcohols, such as sugar, combination takes place very slowly. The behaviour of ethyl metaphosphate towards ammonia and its derivatives has also been studied. It is found that ammonia and primary amines yield derivatives of iminophosphoric acid,  $\text{NH}[\text{PO}(\text{OEt})\cdot\text{OH}]_2$  and



while secondary amines and primary bases containing strongly acid groups in the molecule (carbamide and aminodicarboxylic acids) are converted into derivatives of ethyl aminophosphoric acid of the types  $\text{RR}'\cdot\text{PO}(\text{OEt})\cdot\text{OH}$  and  $\text{NHR}\cdot\text{PO}(\text{OEt})\cdot\text{OH}$  respectively; tertiary

amines yield salts having the constitution  $\text{Q} \rightarrow \text{PO}\cdot\text{OEt}$ .

When shaken with ethyl metaphosphate in chloroform solution at the ordinary temperature, aminomonocarboxylic acids give rise to readily soluble derivatives of diethyl iminopyrophosphate, whereas aminodicarboxylic acids remain unchanged. Serine unites with three



molecules of ethyl metaphosphate, of which two are easily removed by boiling with water and lead carbonate. It is suggested that the separation of amino-acids might be effected by utilising these differences in their behaviour towards the ester.

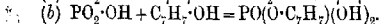
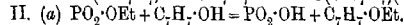
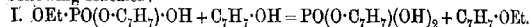
\* Details of the preparation of ethyl metaphosphate from silver metaphosphate and ethyl iodide, and also by the interaction of phosphoric oxide and diethyl ether, are given. The ester may also be obtained by heating diethyl hydrogen orthophosphate under diminished pressure at  $80^{\circ}$ ; at higher temperatures, triethyl orthophosphate is produced. Diethyl hydrogen orthophosphate is readily prepared by the interaction of ethyl metaphosphate and alcohol in molecular proportions at the ordinary temperature.

\* When metaphosphoric acid is heated with alcohol and the resulting solution treated with water and barium hydroxide, barium ethyl orthophosphate,  $C_2H_5O_4PBa \cdot H_2O$ , and barium diethyl orthophosphate,  $Ba(C_2H_5O_4P)_2$ , are produced; the separation of these two salts is accomplished by taking advantage of the greater solubility of the latter in aqueous alcohol.

\* Ethyl metaphosphate reacts with water at the ordinary temperature to form *diethyl dihydrogen pyrophosphate*, which gives an amorphous barium salt,  $C_4H_{10}O_7P_2Ba$ .

Molecular quantities of ethyl metaphosphate and ethylene chlorohydrin, when kept for three to four days at the ordinary temperature, yield *ethyl chloroethyl hydrogen orthophosphate*, which was isolated in the form of its barium salt,  $Ba(C_2H_5O_4ClP)_2$ . When ethyl metaphosphate is heated on the water-bath with excess of ethylene chlorohydrin, a mixture of diethyl hydrogen orthophosphate and ethyl chloroethyl hydrogen orthophosphate is produced.

Benzyl alcohol reacts with ethyl metaphosphate in boiling chloroform solution, yielding benzyl ethyl ether and dibenzyl ether, together with *benzyl dihydrogen phosphate* and *ethyl benzyl hydrogen phosphate*, the reaction taking place according to one or both of the following schemes:



The two esters were isolated in the form of their barium salts,  $C_6H_5O_4P_2Ba \cdot 2H_2O$  and  $Ba(C_6H_5O_4P)_2$ .

*Ethyl choline phosphate* is obtained as a hygroscopic, glassy mass by treating ethyl chloroethyl hydrogen orthophosphate with trimethylamine in alcoholic solution; the yellow, amorphous *platinichloride* was analysed.

*Glycerolphosphoric acid* is prepared by heating ethyl metaphosphate with excess of glycerol; the barium salt has the composition  $C_3H_5O_6P_2Ba \cdot 1\frac{1}{2}H_2O$ .

When allyl iodide, diluted with chloroform, is shaken with equal molecular quantities of silver metaphosphate and ethylene chlorohydrin, allyl phosphate and *allyl chloroethyl hydrogen orthophosphate*, are produced. The barium salt of the last-named compound has the composition  $Ba(C_3H_5O_4ClP)_2$ .

\* The compounds of ethyl metaphosphate with ammonia,  $C_4H_{10}O_6N_2P_2$ ,

ethylamine,  $C_{10}H_{20}O_8N_2P_2$ , diethylamine,  $C_{10}H_{22}O_8N_2P$ , and with triethylamine,  $C_{18}H_{30}O_8NP$ , are all syrups, which solidify to glasses when kept in a desiccator under diminished pressure.

The compound with carbamide,  $C_8H_{10}O_8N_4P$ , is hydrolysed when boiled with water into carbamide and ethyl dihydrogen phosphate.

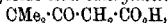
Aspartic acid and glutamic acid react slowly with ethyl metaphosphate in boiling chloroform solution, yielding glassy substances of the composition  $C_8H_{12}O_7NP$  and  $C_7H_{11}O_7NP$  respectively.

The compounds with alanine,  $C_7H_{17}O_8NP_2$ , valine,  $C_8H_{21}O_8NP_2$ , and leucine,  $C_{10}H_{25}O_8NP_2$ , were obtained in the form of glassy masses, which are decomposed when boiled with water into ethyl dihydrogen phosphate, phosphoric acid, and the corresponding amino-acid. The leucine derivative gives with diethylamine a salt,  $C_{22}H_{40}O_8N_4P_2$ , containing three molecules of diethylamine.

The compound of ethyl metaphosphate with serine has the composition  $C_6H_{22}O_{12}NP_5$ . F. B.

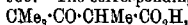
**$\alpha\beta$ -Dimethyl-lævulic Acid.** RICHARD WILLSTÄTTER and ALESSANDRO BROSSA (*Ber.*, 1911, 44, 2191—2194).— $\alpha\beta$ -Dimethyl-lævulic acid,  $COMe\cdot CHMe\cdot CHMe\cdot CO_2H$ , required for comparative purposes in connexion with the degradation of phytol, has been obtained from alcoholic sodium ethoxide and equimolecular quantities of methyl  $\alpha$ -bromopropionate and methyl methylacetoacetate, whereby mixtures of the methyl and ethyl esters of  $\alpha\beta$ -dimethylsuccinic acid and of acetyldimethylsuccinic acid are obtained. The hydrolysis of the latter by 8% barium hydroxide yields a mixture of  $\alpha\beta$ -dimethylsuccinic acid and the acid required.  $\alpha\beta$ -Dimethyl-lævulic acid has b. p.  $120^\circ/5$  mm.,  $145^\circ/12$  mm., and  $D_4^{20}$  1.112, and forms an ethyl ester, b. p.  $90^\circ/9$  mm.,  $D_4^{20}$  0.939, *p*-nitrophenylhydrazone, m. p.  $121$ — $123^\circ$  (decomp.), and anhydride, b. p.  $114^\circ/16$  mm.,  $235$ — $237^\circ/727$  mm.,  $D_4^{20}$  1.084. C. S.

**Ethyl tert.-Valerylacetate.** ERIK WAHLBERG (*Ber.*, 1911, 44, 2071—2076).—Attempts to prepare ethyl tert.-valerylacetate,  $CM_3\cdot CO\cdot CH_2\cdot CO_2Et$ , by the interaction of magnesium tert.-butyl iodide and ethyl cyanoacetate, and also by the removal of carbon monoxide from ethyl trimethylacetylpyruvate, proved fruitless. The ester is obtained in small yield by the condensation of pinacolin with ethyl carbonate by means of sodium ethoxide or sodamide. It is best prepared by heating an aqueous solution of tert.-valerylacetimino-ether hydrochloride at  $50$ — $60^\circ$  (see this vol., i, 702). It is a colourless liquid, b. p.  $96$ — $97^\circ/15$  mm.,  $D_4^{20}$  0.967, giving an intense violet coloration with ferric chloride. When hydrolysed with aqueous potassium hydroxide it yields tert.-valerylacetic acid,



which has m. p.  $47$ — $49^\circ$ , and decomposes at  $100^\circ$  into pinacolin and carbon dioxide.

**Ethyl tert.-valerylmethylacetate** or **ethyl  $\gamma\gamma\gamma$ -tetramethylacetoacetate**,  $CM_3\cdot CO\cdot CHMe\cdot CO_2Et$ , prepared by the successive action of sodium ethoxide and methyl iodide on the above ester, is an oil, b. p.  $93$ — $94^\circ/15$  mm.,  $D_4^{20}$  0.955. The corresponding acid,



crystallises in small, lustrous plates, which have m. p. 100—101°, and simultaneously decompose into carbon dioxide and ethyl *tert.*-butyl ketone.

1-Phenyl-3-*tert.*-butyl-5-pyrazolone,  $C_{15}H_{16}ON_2$ , prepared by the interaction of phenylhydrazine and ethyl *tert.*-valerylacetate, crystallises from benzene in large leaves, m. p. 110.5—111.5°, and when oxidised with ferric chloride in alcoholic solution yields *bisphenyl*-*tert.*-butylpyrazolone,  $C_{26}H_{30}O_2N_2$ , m. p. above 290°.

1-Phenyl-4-methyl-3-*tert.*-butyl-5-pyrazolone,  $C_{14}H_{18}ON_2$ , prepared from phenylhydrazine and ethyl  $\alpha\gamma\gamma$ -tetramethylacetoacetate, has m. p. 114.5—115.5°.

Ethyl  $\alpha\gamma\gamma\gamma$ -pentamethylacetoacetate,  $CM_3\cdot CO\cdot CM_3\cdot CO_2Et$ , obtained from ethyl tetramethylacetoacetate by the successive action of sodium ethoxide and methyl iodide, has b. p. 98.5—99°/15 mm., and on hydrolysis with dilute sulphuric acid yields pentamethylacetone. When heated with phenylhydrazine, it gives 1-phenyl-4:4-dimethyl-3-*tert.*-butyl-5-pyrazolone in an impure condition, m. p. 107—108°.

F. B.

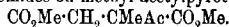
**Ketoglutaric Acids and the Acid-aldehydes of the Succinic Series.** EDMOND E. BLAISE (*Compt. rend.*, 1911, 153, 71—73).—When ethyl oxalopyrotartrate is saturated with hydrogen bromide at 0°, and allowed to remain for some weeks, crystals are obtained, together with a viscous liquid. The latter is esterified and distilled, when three fractions are obtained: (1) A liquid, b. p. 143—145°/15 mm., which consists principally of an ester of the above-mentioned crystalline

substance; on hydrolysis it forms the lactone,  $\begin{matrix} CHMe\cdot CH \\ \diagdown \quad \diagup \\ CO \quad O \end{matrix} > C\cdot CO_2Et$ , and when treated with barium hydroxide it yields the aldehyde,  $CO_2Et\cdot CHMe\cdot CH_2\cdot CHO$ , b. p. 89—90°/18 mm. The latter forms a semicarbazone, m. p. 110.5°, a *p*-nitrophenylhydrazone, m. p. 89°, an oxime, b. p. 137—138°/16 mm., and an azine,  $CHMe\cdot \begin{matrix} CH=N \\ \diagdown \quad \diagup \\ CH_2 \quad CO \end{matrix} > NH$ , m. p. 66°, b. p. 134—136°/18 mm. (2) The foregoing aldehyde. (3) An ethoxylactone,  $\begin{matrix} CHMe-CH_2 \\ \diagdown \quad \diagup \\ CO \quad CH(OEt) \end{matrix} > O$ , having b. p. 101°/18 mm.

The acid-aldehyde,  $CO_2H\cdot CHMe\cdot CH_2\cdot CHO$ , has b. p. 139—140°/12.5 mm.; the semicarbazone, m. p. 195°; the oxime, m. p. 77°; the *p*-nitrophenylhydrazone has m. p. 198°; the phenylhydrazone, m. p. 71—72°, and on distillation forms an azine, m. p. 42°, b. p. 183—185°/12 mm.

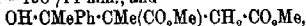
W. O. W.

**Action of Organo-magnesium Compounds on Methyl Acetylpyrotartrate.** PHILIPPE BARBIER and RÉNÉ LOCQUIN (*Bull. Soc. chim.*, 1911, [iv], 9, 717—722).—An attempt was made to prepare acids of the type  $OH\cdot CRE\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$  by the action of magnesium alkyl bromides on methyl acetylpyrotartrate,



The esters alone could be obtained, however, the only products on saponification being pyrotartaric acid and the corresponding ketone,  $R\cdot COMe$ .

The authors tried magnesium isobutyl bromide and magnesium phenyl bromide, and obtained from these respectively the compounds  $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CMe}(\text{OH}) \cdot \text{CMe}(\text{CO}_2\text{Me}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$ , an oily liquid, b. p. 157—158°/14 mm., and

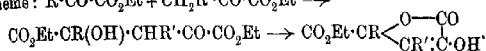


a light-coloured, odourless oil, which decomposed on distillation even under reduced pressure.

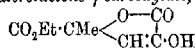
The experiments furnish a new method of preparing ketones containing the group COMe. W. G.

**A New Method of Obtaining Glycuronic Acid.** ADOLF JOLLES (*Biochem. Zeitsch.*, 1911, 34, 242—247\*).—The acid was obtained by the oxidation of 2% dextrose solution by hydrogen peroxide. After destruction of the excess of the latter by platinum-black, the acid was precipitated by basic lead acetate. It was identified by the isolation of the *p*-bromophenylhydrazine derivative, and by oxidation to saccharic acid. S. B. S.

**Lactonisation of  $\alpha$ -Ketonic Esters.** HENRI GAULT (*Compt. rend.*, 1911, 153, 107—110).— $\alpha$ -Ketonic esters of mono- and of dicarboxylic acids under the influence of amines, sulphuric acid, or, best of all, sodium ethoxide undergo condensation in accordance with the scheme:  $\text{R} \cdot \text{CO} \cdot \text{CO}_2\text{Et} + \text{CH}_2\text{R}' \cdot \text{CO} \cdot \text{CO}_2\text{Et} \rightarrow$



The products are viscous liquids, which cannot be distilled without decomposition, dissolve in alkali carbonates or hydrogen carbonates, develop violet-red colorations with ferric chloride, and form acyl derivatives; with the exception of the substance obtained from ethyl pyruvate, they do not react in the ketonic forms; thus ethyl pyruvate yields *ethyl  $\alpha$ -keto- $\gamma$ -valerolactone- $\gamma$ -carboxylate*,



(*phenylhydrazone*, m. p. 120—121°; *semicarbazone*, m. p. 220°), whilst ethyl  $\alpha$ -ketosuccinate,  $\alpha$ -ketoglutarate, and  $\alpha$ -ketoadipate respectively yield substances in which R is  $\text{CH}_3 \cdot \text{CO}_2\text{Et}$ ,  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , and  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$  respectively, and R' is  $\text{CO}_2\text{Et}$ ,  $\text{CH}_2 \cdot \text{CO}_2\text{Et}$ , and  $\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$  respectively. C. S.

**Chemical Action of Light.** II. G. INGHILLERI (*Zeitsch. physiol. Chem.*, 1911, 73, 144—151).—The formation of a sugar, m. p. 98°, by the action of light on a mixture of 40% formaldehyde solution and crystallised oxalic acid in sealed tubes has been confirmed (compare this vol., i, 354). Formaldehyde itself (40% solution) when similarly exposed yields a yellow, syrupy liquid, but when mixed with water and then exposed to sunlight a yellow syrup, methyl alcohol, and formic acid are formed, the two latter probably by the action of the alkali of the glass on the formaldehyde. A mixture of methyl alcohol and formaldehyde (40%) under similar conditions yields methyl formate. Tubes containing glycerol, oxalic acid, and a little water

\* and *Monatsh.*, 1911, 33, 623—629.

gave a yellow oil containing glyceryl monobutyrate, together with a liquid containing butyric acid: J. J. S.

**Viscose from Cellulose and from Starch.** HERMANN OST, F. WESTHOFF, and L. GESSNER (*Annalen*, 1911, 382, 340—360).—Starch yields a viscose similar to that obtained from cellulose, but it is more stable, and allows the process of "ripening" to be studied more readily. To obtain the viscose, 10 grams of potato starch are suspended in 20—25 c.c. of carbon disulphide in a stoppered bottle, the mixture is shaken, and at least 2 mols. of sodium hydroxide are added at once in the form of 10—20% aqueous solution. After some hours, a yellow jelly is obtained, which can be drawn out in the form of slender threads. This xanthate dissolves in water to a viscous liquid, from which alcohol or saturated saline solutions precipitate the xanthate as a leather-like mass. Mineral acids and concentrated acetic acid yield starch, carbon disulphide, and hydrogen sulphide. When kept, the viscose becomes thinner, it "ripens," but, even after months, coagulation is not observable. Very dilute alkali and an excess of very concentrated (50%) alkali do not yield a viscose.

The products, after purification by repeated solution in water and precipitation by alcohol, were analysed, the sodium was estimated as sodium sulphate, the sulphur estimated by oxidation by Carius' method, as Cross's method of oxidation with hypochlorite gave low results, and the starch estimated by decomposing with acid, hydrolysing to dextrose, and estimating this by means of Fehling's solution.

The composition of different samples varied appreciably, mainly owing to hydrolysis, which takes place during solution and precipitation. In most cases for 1 mol. of starch, 1.35—1.25 atoms of S and 1.3—1.2 atoms of Na were found. The formula suggested for the xanthate is  $(\text{ONa} \cdot \text{C}_6\text{H}_8\text{O}_3 \cdot \text{O} \cdot \text{CS} \cdot \text{SNa})_n$ , but owing to hydrolysis, which can take place according to the two equations:

(1)  $(\text{ONa} \cdot \text{C}_6\text{H}_8\text{O}_3 \cdot \text{OCS}_2\text{Na})_n + n\text{H}_2\text{O} = (\text{C}_6\text{H}_9\text{O}_4 \cdot \text{OS}_2\text{Na})_n + n\text{NaOH}$ , and (2)  $(\text{C}_6\text{H}_9\text{O}_4 \cdot \text{OCS}_2\text{Na})_n + n/2 \cdot \text{H}_2\text{O} = (\text{C}_{12}\text{H}_{19}\text{O}_9 \cdot \text{OCS}_2\text{Na})_{n/2} + n/2 \cdot \text{CS}_2 + n/2 \cdot \text{NaOH}$ , the percentages of sulphur and sodium are low.

During the process of ripening, the viscose becomes less and less viscous; for example, a specimen purified by three precipitations with alcohol, when dissolved in water and examined in an Engler's viscometer at 20°, had a viscosity of 130, but this fell within twenty-five days to 9. The ripening is accompanied by hydrolysis similar to that which occurs during purification, but to a greater extent. After keeping crude viscose for twelve days and then purifying by three precipitations with alcohol, the number of atoms of sulphur and sodium compared with 1 mol. of starch had fallen to 0.34 and 0.29 respectively, whereas the numbers for the fresh viscose were 1.77 and 1.82. The diminution in the viscosity is not due to this hydrolysis, but to the action of the alkali on the starch, that is, to a diminution of the value  $n$ . This is supported by the fact that soluble starch and dextrans of high molecular weight yield comparatively mobile xanthates.

Viscose from cellulose also undergoes hydrolysis during purification and ripening. During the latter process its viscosity first diminishes

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and then increases again, the final increase being due to the colloidal separation of free cellulose.

The cellulose deposited from an old specimen of viscose by means of hydrochloric acid is apparently identical with the cellulose obtained from alkali cellulose, and its composition is practically that of cellulose, provided the specimens are thoroughly dehydrated at 120—125°.

An erythro-dextrin obtained by the action of malt extract on starch paste at 70° has practically no reducing properties, and differs but little from starch in composition.

J. J. S.

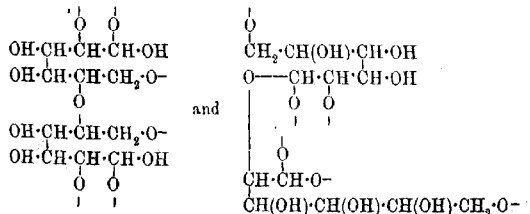
**Acid Hydrolysis of Starch Granules.** CHESTER B. DURYEA (*J. Soc. Chem. Ind.*, 1911, 30, 789—790).—It has been demonstrated experimentally that maltose is formed quite early in the hydrolysis of maize starch granules by hydrochloric acid; in fact, it is not improbable that it is an initial product of the hydrolysis of starch. It would also appear that the production of maltose is accompanied by a general simplification of the molecular condition of the carbohydrates composing the granules; in other words, the production of each successive molecule of maltose leads to the formation of a simpler dextrin.

W. H. G.

**Observations on Cotton and Nitrated Cotton.** HENRY DE MOSENTHAL (*J. Soc. Chem. Ind.*, 1911, 30, 782—786).—Attempts to dialyse solutions of nitrocellulose in acetone, making use of the bladder of the sturgeon and also parchment paper, have led to the conclusion that, contrary to the author's earlier statements (*ibid.*, 1904, 23, 292; 1907, 26, 443), nitrocellulose does not dialyse. Further, solutions of nitrated cotton in acetone do not give any indication of a pressure in a Pfeffer osmometer with various septa.

The absorption spectra of a number of solutions of cellulose nitrates and acetates were investigated; in all cases a continuous spectrum was observed, which showed a shortening in the ultra-violet progressing with the concentration; it may be assumed therefore that the cellulose group absorbs ultra-violet light.

The author inclines to the view that the dextro-cellulose of cotton is an aliphatic compound of a polysaccharide character, most suitably represented by open formulæ derived from the ring formulæ of Green and of Vignon, such as:



The latter formula seems preferable, since the monose groups are connected by acetal linkings only, which would account for the ease

with which cellulose is hydrolysed and also the formation of a large number of celluloses and hydrocelluloses by the addition of water.

W. H. G.

**Acetylation of Cotton Cellulose.** CARL G. SCHWALBE (*Zeitsch. angew. Chem.*, 1911, 24, 1256—1260).—It has been shown previously (compare Abstr., 1910, i, 224) that the cellulose acetates obtained by the processes of Bayer (D.R.-P. 159524) and of Lederer (D.R.-P. 163316) are acetates of hydrocelluloses. The present communication contains the results of experiments performed with the object of ascertaining at which stage of the process the hydrolysis of the cellulose occurs. It is found that the first product of the interaction of cotton cellulose with acetic anhydride and acetic acid in the presence of sulphuric acid is an acetate of a cellulose derivative capable of reducing Fehling's solution (hydrocellulose). As the reaction proceeds, however, cellulose acetates are formed, which, when hydrolysed, yield cellulose derivatives incapable of reducing boiling alkaline copper solutions; in agreement with this, it is found that the product first formed in the Lederer process (acetylation of hydrocellulose) consists of acetates of a cellulose derivative which does not reduce Fehling's solution. Towards the end of the reaction, acetates of hydrocelluloses again appear, and, as already stated, the final product consists almost solely of acetates of a hydrocellulose.

Evidence is also brought forward to show that the acetylation of the hydrocellulose initially produced proceeds at a far greater rate than the formation of the hydrocellulose itself from the cotton cellulose.

It is evident from the results now recorded that the hydrolysis which takes place during acetylation cannot be regarded as a tertiary process, as stated by Jentgen (compare this vol., i, 115).

W. H. G.

**Cellulose. Hydrocellulose.** CARL G. SCHWALBE (*Zeitsch. angew. Chem.*, 1911, 24, 1260—1262. Compare this vol., i, 115).—Polemical. A reply to Jentgen (this vol., i, 355).

W. H. G.

**Cellulose Acetate.** HERMANN OST (*Zeitsch. angew. Chem.*, 1911, 24, 1304—1306, 1307).—Historical. The author claims to have been the first to show that the cellulose acetate obtained by the processes of Bayer and of Lederer is a cellulose triacetate.

W. H. G.

**Cellulose Acetate.** ARTHUR EICHENGRÜN (*Zeitsch. angew. Chem.*, 1911, 24, 1306—1307).—Polemical. A reply to Ost (compare preceding abstract).

W. H. G.

**Thioamides: Formation of Thiopolypeptide Derivatives by the Action of Hydrogen Sulphide on Aminoacetonitrile.** TREAT B. JOHNSON and GERALD BURNHAM (*J. Biol. Chem.*, 1911, 9, 449—462).—Aminoacetonitrile reacts normally with hydrogen sulphide

at the ordinary temperature, giving the unknown thioamide of glycine, which, however, was not isolated. It is very unstable, and decomposes spontaneously in alcoholic solution to the thiopoly peptide derivative, *thioglycylglycinethioamide*,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CS}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CS}\cdot\text{NH}_2$ . In part this thioamide undergoes an inner condensation with loss of ammonia, forming a *dithiopiperazine*,  $\text{NH}\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CS} \\ \text{CS}\cdot\text{CH}_2\end{smallmatrix}\rangle\text{NH}$ . This

cyclic derivative is the chief product of the reaction; it dissolves in cold alkali hydroxide and has no basic properties. Hydrochloric acid hydrolyses it to glycine hydrochloride and hydrogen sulphide.

*2:5-Dithiopiperazine* turns brown at about  $160^\circ$ , and black at  $270$ – $280^\circ$ ; the *lead* and *mercury* salts are light brown; the *silver* salt separates in a gelatinous condition, and begins to decompose at once with the formation of black silver sulphide.

*Thioglycylglycinethioamide* is a dark brown powder, m. p.  $89$ – $95^\circ$  (decomp.). E. F. A.

The Rules of Substitution in the Benzene Nucleus. ARNOLD H. HOLLEMAN (*Bull. Soc. chim.*, 1911, [iv], 9, i–xlv).—A lecture delivered before the French Chemical Society. W. G.

The Study of Isomorphous Sulphonic Derivatives of Benzene. HENRY A. MIERS, HENRY E. ARMSTRONG, WILLIAM J. POPE, and WILLIAM P. WYNNE (*Brit. Assoc. Reports*, 1910, 100).—This report refers to the results obtained by the examination of twenty-nine derivatives of the 1:4 series (Barlow and Pope, *Trans.*, 1910, 97, 2308), and which are found to be in accordance with Barlow and Pope's theory correlating molecular structure with crystalline form. T. S. P.

Benzylindene. RUDOLF WEISSGERBER (*Ber.*, 1911, 44, 2216).—Benzylindene was described in 1906 by Thiele, who showed that Marckwald's so-called benzylindene was really dibenzylindene accompanied by a little viscous oil. The author has succeeded in solidifying this oil, and shows that it is identical with his benzylindene, m. p.  $33$ – $34^\circ$ . C. S.

The Transformation of Aromatic Nitroamines and Allied Substances, and its Relation to Substitution in Benzene Derivatives. FREDERIC S. KIPPING, KENNEDY J. P. ORTON, SIEGFRIED RUEHMANN, ARTHUR LAPWORTH, and JOHN T. HEWITT (*Brit. Assoc. Reports*, 1910, 85–99).—This report [with William J. Jones] deals with the chlorination of anilides and the transformation of acylchloroaminobenzenes, and with the bromination of anilides and the conversion of bromoamines. T. S. P.

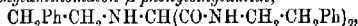
Two New Forms of 2-Nitro-6-hydroxylaminotoluene. KURT BRAND (*Ber.*, 1911, 44, 2045–2047).—When crude nitrohydroxylaminotoluene prepared by electrolysis (compare Brand and Zöller, *Abstr.*, 1907, i, 755) is dissolved in boiling benzene, it first crystallises in slender, yellow needles, changing to a stable, almost colourless form, which differs from the stable, short, yellow crystals previously



described. Three forms, two stable and one unstable, of nitro-hydroxylaminotoluene therefore exist. The unstable form has not yet been separated pure from benzene. It is converted into either of the stable forms on inoculation. Further, solutions of either of the stable forms in hot benzene, inoculated with a crystal of the other form and allowed to cool slowly, yield the other form, or in some cases a mixture of the two stable forms. The stable yellow form has m. p. 117—117.5°; the colourless form becomes yellow at 105° and melts at 115° or 117—117.5°, the former figure applying to an incompletely converted sample. E. F. A.

**Condensation of a Substituted Formamide to a Derivative of Aminomalonalonamide.** HERMANN DECKER and PAUL BECKER (*Annalen*, 1911, 382, 369—377).—The formyl derivative of phenylethylamine (Bischler and Napieralski, *Abstr.*, 1893, i, 608) reacts with phosphoric oxide or zinc chloride, yielding a product identical with that obtained by Decker and Kropp (*Abstr.*, 1909, i, 513) by the action of phosphorus pentachloride and aluminium chloride. The product is a phosphate of the base  $C_{27}H_{31}O_2N_3$ , and has been obtained in a crystalline form. As the base is mono-acid and on hydrolysis loses two molecules of  $\beta$ -phenylethylamine and one of carbon dioxide, yielding  $\beta$ -phenylethylglycine, which can be synthesised from chloroacetic acid and  $\beta$ -phenylethylamine, the conclusion is drawn that it is  $\beta$ -phenylethylaminomalondiphenylethylamide. A strong odour of  $\beta$ -phenylethylcarbylamine is noticed during the condensation, and it is possible that the carbylamine is an intermediate product in the formation of the base.

*$\beta$ -Phenylethylaminomalon- $\beta$ -phenylethylamide,*

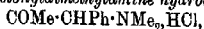


yields a *phosphate*, which crystallises from 95% alcohol in slender, colourless needles, m. p. 176—178°. The *picrate*,  $C_{33}H_{34}O_9N_6$ , separates from alcohol in well-developed crystals, m. p. 192°. The *hydrochloride*,  $C_{27}H_{31}O_2N_3 \cdot HCl$ , crystallises from 80% alcohol containing hydrogen chloride in colourless plates, m. p. 184—186°, and the *platinichloride*,  $2C_{27}H_{31}O_2N_3 \cdot H_2PtCl_6$ , crystallises from alcohol in yellowish-red, glistening plates, m. p. 254—255°. The free base, obtained by the action of ammonia on the picrate, crystallises from 80% alcohol in slender needles, m. p. 85°. Both the base and its salts have an extremely bitter taste. When the base is hydrolysed with 15% hydrochloric acid and alcohol,  *$\beta$ -phenylethylglycine hydrochloride*,  $CH_2Ph \cdot CH_2 \cdot NH \cdot CH_2 \cdot CO_2H \cdot HCl$ , is formed. It crystallises from dilute acid in colourless plates, m. p. 243—244° (decomp.) when rapidly heated.  *$\beta$ -Phenylethylglycine*,  $CH_2Ph \cdot CH_2 \cdot NH \cdot CH_2 \cdot CO_2H$ , crystallises from 80% alcohol in slender, colourless needles, m. p. 274—276°, and dissolves readily in acids and alkalis.

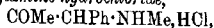
Alcoholic potassium hydroxide solution also hydrolyses the base in a similar manner. J. J. S.

**Doubly Linked Carbon Atoms and the Carbon-Nitrogen Linking.** VIII. Reduction of *N*-Alkylated Amino-ketones. HERMANN ENDE and ERNST RUNNE (*Arch. Pharm.*, 1911, 249, 354—370. Compare this vol., i, 281).— *$\alpha$ -Phenylacetonyltrimethylammonium bromide*,

$\text{COMe}\cdot\text{CHPh}\cdot\text{NMe}_2\cdot\text{Br}$ , an oil obtained from  $\alpha$ -bromo- $\alpha$ -phenylacetone and 33% alcoholic trimethylamine in a freezing mixture, has been converted into the *aurichloride*, m. p. 158—159°, and the *platinichloride*, m. p. 207—208° (decomp.). The corresponding chloride is not attacked by zinc and dilute sulphuric acid, and is decomposed by sodium amalgam and dilute hydrochloric acid at 0°, yielding trimethylamine and phenylacetone (a portion of which is reduced to the carbinal).  *$\alpha$ -Phenylacetonyldimethylamine hydrochloride*,

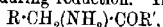


m. p. 193—195°, ultimately obtained from  $\alpha$ -bromo- $\alpha$ -phenylacetone and dimethylamine in cold benzene, is converted into  $\alpha$ -phenylacetone and dimethylamine by sodium amalgam in faintly acid solution.  *$\alpha$ -Phenylacetonylmethylamine hydrochloride*,



m. p. 210—211° (decomp.), obtained in a similar manner by means of methylamine, is only decomposed to a small extent by sodium amalgam in acid solution, the chief product being  *$\alpha$ -methylamino- $\alpha$ -phenylisopropyl alcohol*,  $\text{NHMe}\cdot\text{CHPh}\cdot\text{CHMe}\cdot\text{OH}$ , a yellow oil which forms a *hydrochloride*, m. p. 191—193°, and a *platinichloride*, m. p. 193—194° (decomp.). Betaine hydrochloride is scarcely attacked by sodium amalgam.

From these and from numerous other examples quoted from the literature, the authors state that the carbonyl group (carbon-oxygen double linking), except when present in a carboxyl group, diminishes, even to a greater extent than does the carbon double linking under otherwise the same conditions, the stability of a neighbouring single carbon-nitrogen linking during reduction. In a substance,



three factors exert an influence in weakening the carbon-nitrogen linking, namely, carbon double linkings in R, the carbonyl group, and the loading of the amino-group with methyl groups; the influence of the last factor is very slight for primary and secondary amino-groups (Abstr., 1909, i, 708, 709).

C. S.

**Contradiction of E. Büllmann's Interpretation of Homochromoisomerism as Polymorphism.** ARTHUR HANTZSCH (*Ber.*, 1911, 44, 2001—2009).—Polemical (compare Hantzsch, Abstr., 1910, i, 474; Büllmann, this vol., i, 367). The author upholds his contention that the two phenylmethylpicramides are isomeric and not polymorphic.

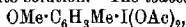
E. F. A.

***o*- and *m*-Iodo-*p*-tolyl Methyl Ether and Derivatives with Multivalent Iodine.** CARL WILLGERODT and RUDOLPH SCHLOSS (*Ber.*, 1911, 44, 1708—1711).—A mixture of *m*- and *o*-iodo-*p*-tolyl methyl ethers is obtained by boiling a glacial acetic acid solution of *p*-tolyl methyl ether with iodine chloride until hydrogen chloride ceases to be evolved, then pouring into water, and shaking with sulphurous acid. The *o*-iodo-compound has b. p. 237—238° (compare Schall and Dralle, Abstr., 1885, 146), and the *meta*-compound,  $\text{C}_6\text{H}_4\text{IMe}\cdot\text{OMe}$ , crystallises from dilute alcohol in colourless, rhombic plates, m. p. 75°. *p*-Tolyl methyl ether *o*-iododichloride,  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{ICl}_2$ , separates from light

petroleum in yellow needles, which decompose rapidly on exposure to the air, regenerating the original iodo-compound.

*Phenyl-p-methoxy-o-tolylodanum iodide*,  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{IPhI}$ , obtained from the iodo-dichloride and mercury diphenyl in the presence of a few drops of water, and subsequent treatment with potassium iodide, crystallises from alcohol in pale yellow needles, m. p.  $181^\circ$ .

*p-Tolyl methyl ether m-iododichloride*,  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{ICl}_2$ , forms orange-yellow, felted needles, decomposing at  $58-60^\circ$ . The corresponding *iodoso*-compound,  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{IO}$ , forms a pale yellow, amorphous powder, which decomposes at  $176^\circ$ . It does not yield the corresponding iodoxy-compound when warmed with water or treated with sodium hypochlorite solution. The *iodosuccinate*,



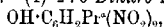
forms long, glistening crystals, m. p.  $120-122^\circ$ , and *phenyl-p-methoxy-m-tolylodanum iodide*,  $\text{C}_{11}\text{H}_{14}\text{OI}_2$ , crystallises from alcohol, and has m. p.  $166^\circ$ .

J. J. S.

#### Products of the Action of Nitric Acid on Dihydroanethole.

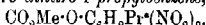
HERMANN THOMS and W. DRAUZZBURG (*Ber.*, 1911, 44, 2125-2133).—

When heated with 45% nitric acid, dihydroanethole (*p*-methoxypropylbenzene) yielded the following products: (1) Anisic acid. (2) Anisaldehyde. (3) 3-Nitro-4-methoxypropylbenzene,  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Pr}\cdot\text{NO}_2$ , which is an almost colourless liquid, b. p.  $164-169/9$  mm., solidifying at  $-6^\circ$ ; it is oxidised by potassium permanganate and dilute sulphuric acid to 3-nitroanisic acid. (4) 2:6-Dinitro-4-propylphenol,



which crystallises from ether in yellow, prismatic columns, m. p.  $46^\circ$ ; the sodium salt forms dark reddish-green needles, which sinter at  $264^\circ$  and decompose explosively; the potassium and silver salts are also mentioned. The acetyl derivative crystallises in greenish-yellow needles, m. p.  $89^\circ$ ; the benzoyl derivative has m. p.  $86.5-87^\circ$ . When heated with diphenylcarbonyl chloride and pyridine, the dinitrophenol yields a diphenylurethane,  $\text{NPh}_2\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_3\text{Pr}\cdot(\text{NO}_2)_2$ , crystallising in cubes, m. p.  $136.5^\circ$ .

#### 4-Methylcarbonato-3:5-dinitro-1-propylbenzene,



prepared by the action of methyl chlorocarbonate on the sodium salt, crystallises in almost white needles, m. p.  $85.5-86.5^\circ$ .

The dinitrophenol is reduced by tin and hydrochloric acid to 2:6-diamino-4-propylphenol, which is unstable in the free condition, and is, therefore, best isolated in the form of the hydrochloride,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Pr}\cdot(\text{NH}_2)_2\cdot 2\text{HCl}$ ; the benzoyl derivative forms rosettes of slender needles, m. p.  $198^\circ$ . 2:6-Diacetylamino-4-propylphenol,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Pr}\cdot(\text{NHAc})_2$ , prepared by the gradual addition of acetic anhydride to a solution of the diamine hydrochloride in the presence of a slight excess of sodium acetate and acetic acid, crystallises in needles, m. p.  $161.5-162^\circ$ . The action of nitrous acid on the diamino-phenol results in the formation of a brown dye.

Since 2:6-dinitro-4-propylphenol is also obtained by nitrating 3-nitro-4-methoxypropylbenzene, it is probable that the latter compound

is formed as an intermediate product in the preparation of the dinitrophenol from dihydroanethole by the action of nitric acid.

The above-mentioned transformations of dihydroanethole and its nitro-derivative into dinitropropylphenol constitute the first recorded examples of the oxidation of the methoxy-group to hydroxyl by means of nitric acid.

F. B.

**The Elimination of Methoxy-groups from Phenolic Ethers by means of Nascent Hydrogen.** HERMANN THOMS and W. SIEBELING (*Ber.*, 1911, 44, 2134—2136).—The action of sodium on pyrogallol trimethyl ether in alcoholic solution leads to the formation of resorcinol dimethyl ether, the methoxy-group in position 2 being readily replaced by hydrogen. *iso*Eugenyl methyl ether, when subjected to the same treatment, yields a small quantity of a phenol, whilst in the case of anethole, *m*-methoxypropylbenzene, and asarone no replacement of the methoxy-group was observed.

From these results the authors draw the conclusion that the ready elimination of a methoxy-group from pyrogallol trimethyl ether is due to the accumulation of methoxy-groups in adjacent positions, and not to the presence of a substituent in the para-position (compare Semmler, *Abstr.*, 1908, i, 557, 734; Kostanecki and Lampe, *ibid.*, 442).

F. B.

**Stereoisomeric  $\beta$ -Nitro- $\alpha$ -methoxy- $\alpha\beta$ -diphenylethanes prepared by the Addition of Alkali Methoxide to 7-Nitrostilbene.** FRIEDRICH HEIM (*Ber.*, 1911, 44, 2013—2016. Compare Meisenheimer and Heim, *Abstr.*, 1907, i, 858).—By the interaction of 7-nitrostilbene and sodium methoxide, two stereoisomeric  $\beta$ -nitro- $\alpha$ -methoxy- $\alpha\beta$ -diphenylethanes,  $\text{OMe}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{NO}_2$ , are formed, distinguished as  $\alpha$ , m. p. 130—131°, and  $\beta$ , m. p. 97—98°, modifications (Meisenheimer and Heim, *loc. cit.*). It is now shown that both modifications are formed simultaneously, and that by varying the conditions, one or other is obtained in larger quantity, although the less fusible form always preponderates. The isomerides are separated by crystallisation from light petroleum and mechanical sorting, the  $\alpha$ -form yielding slender, colourless needles, and the  $\beta$ -isomeride stumpy, transparent crystals. The isomerides are precipitated from the reaction mixture either by means of carbon dioxide, which favours the formation of the  $\beta$ -isomeride, or by ammonium chloride and air, a process most favourable to the  $\alpha$ -modification.

On heating above the melting point, the  $\beta$ -isomeride is the more stable, being nearly all recovered after heating at 170°. The  $\alpha$ -isomeride at this temperature becomes dark brown, and liberates fumes with the odour of a nitrile. In neither instance did heating bring about conversion into the other isomeride.

E. F. A.

**Condensation of  $\omega$ -Nitrotoluene with Benzaldehyde. *cis*- and *trans*-7-Nitrostilbene.** FRIEDRICH HEIM (*Ber.*, 1911, 44, 2016—2022).—On condensing benzaldehyde with  $\omega$ -nitrotoluene, in addition to the 7-nitrostilbene obtained by Knoevenagel and Walter (*Abstr.*, 1905, i, 65), m. p. 75°, a second isomeride is formed.

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This separates from light petroleum in darker yellow, stunted crystals, m. p. 128—128.5°, becoming greenish-yellow on exposure to light, and comprises 7—10% of the whole product. Like the isomeride m. p. 75°, it forms a mixture of  $\alpha$  and  $\beta$  nitro- $\alpha$ -methoxy- $\alpha\beta$ -diphenylethane. Each isomeride on heating or distillation is partly converted into the other form.

In addition to these isomerides, three other compounds containing a larger proportion of carbon are formed during the condensation, and separated by distillation of the residue. These are a compound separating in matted, yellow crystals,  $C_{21}H_{17}O_2N$ , a compound  $C_{21}H_{15}ON$ , m. p. 212°, and a compound  $C_{21}H_{13}O_2N_2$ .

This last is probably  $\alpha\gamma$ -dinitro- $\alpha\beta$ -triphenylpropane, formed by the condensation of benzaldehyde with two molecules of  $\alpha$ -nitrotoluene. It separates in slender, colourless, matted crystals, m. p. 177—178.5°.

Concentrated alkali hydroxide eliminates  $NO_2H$ , and converts it into the compound  $C_{21}H_{15}ON$ , m. p. 212°. This compound is also formed by the distillation of 7-nitrostilbene, but it is demonstrated that it is formed during the original condensation. It is regarded as

3:4:5-triphenylisooxazole,  $CPh \begin{smallmatrix} \swarrow CPh \cdot O \\ \searrow CPh \cdot N \end{smallmatrix}$ , and crystallises in slender, colourless needles.

The compound  $C_{21}H_{17}O_2N$  is regarded as  $\alpha$ -nitro- $\alpha\beta$ -triphenylpropylene,  $CH_2Ph \cdot CPh \cdot CPh \cdot NO_2$ ; the yellow, matted needles have m. p. 102—103°. E. F. A.

**Doubly Linked Carbon Atoms and the Carbon-Nitrogen Linking. IX. Arylamino-Alcohols.** HERMANN EMDE and ERNST RUNGE (*Arch. Pharm.*, 1911, 249, 371—382. Compare this vol., i, 714). — $\alpha$ -Amino- $\alpha$ -phenylisopropyl alcohol is obtained in 43.5% yield by treating a 96% alcoholic solution of benzyl methyl ketoxime with sodium amalgam and dilute hydrochloric acid at 0°. Its hydrochloride reacts with methyl iodide and sodium methoxide to form the corresponding trimethylammonium chloride. The decomposition of this chloride by sodium amalgam, or of the corresponding iodide by hydrogen chloride at 170—180°, yields trimethylamine and phenylisopropyl alcohol. *dl*- $\alpha$ -isoEphedrine ( $\alpha$ -methylamino- $\alpha$ -phenylisopropyl alcohol) (this vol., i, 715), in the form of its hydrochloride, decomposes at 250° into benzyl methyl ketone, ammonia, and methyl chloride.  $\alpha$ -Phenyl- $\gamma$ -butanoltrimethylammonium chloride is decomposed by sodium amalgam into  $\alpha$ -phenyl- $\gamma$ -butanol and trimethylamine hydrochloride.

*Methyldiethylhydroxyethylammonium iodide*,  $OH \cdot CH_2 \cdot CH_2 \cdot NMeEt_2I$ , m. p. 249° (decomp.), is obtained by the interaction of hydroxyethyl-diethylamine and methyl iodide in methyl alcohol at 0°. The *platinichloride* and the *aurichloride* decompose at 222—223° and 237—238° respectively; the *chloride* is scarcely attacked by sodium amalgam. C. S.

#### Prep

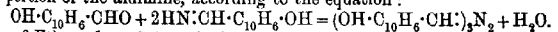
**Ph. Dimeration of Asymmetric Benzyldialkylacetic Acids.** TESNIL (*Compt. rend.*, 1911, 153, 111—113).—The author has

obtained the following substances by Haller and Bauer's method. Phenyl ethyl ketone, methyl iodide, and sodamide (1 mol.) in boiling benzene yield *methyl ethylacetophenone*,  $\text{CH}_3\text{MeEt}\cdot\text{COPh}$ , b. p.  $109^\circ/10$  mm., from which, by a similar process, benzyl chloride produces *benzyl methyl ethylacetophenone*,  $\text{CH}_2\text{Ph}\cdot\text{CMeEt}\cdot\text{COPh}$ , b. p.  $201^\circ/18$  mm. When the last substance is heated with sodamide (1 mol.) and a trace of water in boiling xylene for six hours, it yields benzene and the *amide*,  $\text{CH}_2\text{Ph}\cdot\text{CMeEt}\cdot\text{CO}\cdot\text{NH}_2$ , from which  $\alpha$ -benzyl- $\alpha$ -methylbutyric acid,  $\text{C}_7\text{H}_7\cdot\text{CMeEt}\cdot\text{CO}_2\text{H}$ , b. p.  $180^\circ/18$  mm., m. p.  $31^\circ$ , is obtained by hydrolysis with 50% sulphuric acid at  $150^\circ$ .

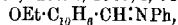
*Ethylpropylacetophenone*,  $\text{CH}_3\text{EtPr}\cdot\text{COPh}$ , b. p.  $138^\circ/19$  mm., and *benzylethylpropylacetophenone*,  $\text{CH}_2\text{Ph}\cdot\text{CEtPr}\cdot\text{COPh}$ , b. p.  $223^\circ/20$  mm., m. p.  $52^\circ$ , are produced in a similar manner. When the latter is treated with sodamide and water in boiling xylene, the chief product is  $\gamma$ -benzylhexane,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{EtPr}$ , b. p.  $117^\circ/18$  mm. The *amide*,  $\text{CH}_2\text{Ph}\cdot\text{CEtPr}\cdot\text{CO}\cdot\text{NH}_2$ , which is only a secondary product, yields  $\alpha$ -benzyl- $\alpha$ -ethylvaleric acid,  $\text{C}_7\text{H}_7\cdot\text{CEtPr}\cdot\text{CO}_2\text{H}$ , b. p.  $200^\circ/18$  mm., by hydrolysis. C. S.

**Ring Formations in the Peri-Position of the Naphthalene Series. IV. Attempts to Prepare a Six-Membered Carbon Ring.** FRANZ SACHS and PERCY BRIGL (*Ber.*, 1911, 44, 2091—2106).—This paper contains an account of unsuccessful attempts to effect the formation of a six-membered carbon ring in the peri-position by the elimination of water from  $\beta$ -2-ethoxy-1-naphthylacrylic acid,  $\beta$ -2-chloro-1-naphthylacrylic acid, and  $\omega$ -2-chloro-1-naphthyl diethyl ketone.

In the preparation of 2-hydroxy-1-naphthaldehyde from  $\beta$ -naphthol, hydrocyanic acid, and hydrochloric acid in ethereal solution in the presence of zinc chloride, a small quantity of *tri-2-hydroxy-1-hydro-naphthamide*,  $(\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH})_3\text{N}_2$ , is produced simultaneously. This crystallises from nitrobenzene in slender, microscopic needles of a bright red colour, m. p.  $312^\circ$ , and is hydrolysed by hydrochloric acid to 2-hydroxy-1-naphthaldehyde and ammonia. The formation of this compound is due to the hydrolytic action of traces of water, whereby a small quantity of the aldimine produced in the reaction is converted into 2-hydroxy-1-naphthaldehyde, which then condenses with a further portion of the aldimine, according to the equation:



2-Ethoxy-1-naphthaldehyde, m. p.  $111^\circ$ , is best prepared by alkylating the hydroxyaldehyde by means of ethyl sulphate in alcoholic solution (compare Bartsch, *Abstr.*, 1903, i, 647). The *anil*,



and *phenylhydrazones* crystallise in light yellow plates, m. p.  $73^\circ$  and  $91^\circ$  respectively; the *semicarbazone*,  $\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_2$ , crystallises from methyl alcohol in long, white needles, m. p.  $214$ — $215^\circ$ .

2-Ethoxy-1-naphthylhydroxyacetone nitrile,  $\text{OEt}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}(\text{OH})\cdot\text{CN}$ , is obtained in an impure condition in the form of large, crystalline plates by the interaction of 2-ethoxy-1-naphthaldehyde and anhydrous hydrocyanic acid in the presence of a small quantity of ammonia. It is exceedingly unstable, and decomposes in solution into its com-

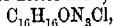
ponents. 2-Ethoxy- $\alpha$ -naphthaldehyde condenses with malonic acid in alcoholic solution in the presence of aniline, yielding  $\beta$ -naphtharoumarin-3-carboxylic acid (compare Bartsch, *loc. cit.*; Knoevenagel and Schröter, Abstr., 1905, i, 63). Attempts to condense the aldehyde with ethyl acetate and ethyl malonate proved unsuccessful.

$\omega$ -2-Trichloro-1-methylnaphthalene,  $C_{10}H_6Cl_3CHCl_2$ , obtained by heating 2-hydroxy-1-naphthaldehyde with phosphorus pentachloride at  $193-205^\circ$ , crystallises from alcohol in rhombic plates, m. p.  $90^\circ$ ; when heated with methyl-alcoholic sodium methoxide it yields 2-chloro-di- $\omega$ -methoxy-1-methylnaphthalene,  $C_{10}H_6ClCH(OMe)_2$ , which crystallises in white prisms capped with small pyramids, m. p.  $86^\circ$ .

2-Chloro-1-naphthaldehyde,  $C_{10}H_6ClCHO$ , prepared by heating the preceding trichloro-compound with dilute acetic acid, or with sodium acetate in aqueous alcoholic solution, crystallises in long, flexible, white needles, m. p.  $76^\circ$ , and gives with strong sulphuric acid a yellow coloration, which becomes blood-red on the addition of nitric acid; the azine,  $C_{22}H_{14}N_2Cl_2$ , forms stout, golden-yellow needles, m. p.  $195^\circ$ , the semicarbazone,  $C_{12}H_{10}ON_3Cl$ , slender, microscopic needles, m. p.  $215^\circ$ . When heated with anhydrous potassium acetate and acetic anhydride at  $170^\circ$ , it yields  $\beta$ -2-chloro-1-naphthylacrylic acid,  $C_{10}H_6ClCH:CHCO_2H$ , which crystallises in long needles, m. p.  $176^\circ$ , and furnishes a crystalline ammonium and an amorphous calcium salt; the salts of the alkali metals and of silver are also mentioned. On account of its instability, the chloride could not be isolated. The amide,  $C_{10}H_6ClCH:CHCO\cdot NH_2$ , crystallises in stout, white needles, m. p.  $195^\circ$ . The acid is reduced by sodium amalgam, chlorine being eliminated from the nucleus at the same time. All attempts to effect an internal condensation in the peri-position by means of sulphuric acid, zinc chloride, or phosphoric oxide were unsuccessful.

Di-2-chloro-1-naphthylideneacetone,  $CO(CH:CH\cdot C_{10}H_6Cl)_2$ , is obtained by condensing 2-chloro-1-naphthaldehyde with acetone by means of strong sulphuric acid. It crystallises from ethyl benzoate in canary-yellow needles, m. p.  $215^\circ$ , and gives with concentrated sulphuric acid an indigo-blue coloration.

$\alpha$ -2-Chloro-1-naphthyl- $\Delta^2$ -penten- $\gamma$ -one,  $C_{10}H_6ClCH:CHCOEt$ , prepared by the condensation of 2-chloro-1-naphthaldehyde and methyl ethyl ketone by means of potassium hydroxide in aqueous alcoholic solution, crystallises in flexible, white needles, m. p.  $74^\circ$ , and gives with strong sulphuric acid a reddish-brown coloration, which almost disappears on the addition of nitric acid; the semicarbazone,



forms lustrous, silky needles, m. p.  $185^\circ$ . When the condensation is carried out in very feebly alkaline solution,  $\alpha$ -2-chloro-1-naphthyl-pentan- $\gamma$ -one- $\alpha$ -ol,  $C_{10}H_6ClCH(OH)CH_2COEt$ , is produced. This crystallises in large double pyramids, m. p.  $124^\circ$ , and is converted by the action of aqueous alcoholic potassium hydroxide into the above-mentioned unsaturated ketone.

$\alpha$ -2-Chloro-1-naphthylpentan- $\gamma$ -one,  $C_{10}H_6ClCH_2CH_2COEt$ , is obtained in the form of a viscid oil by reducing the unsaturated chloro-ketone with aluminium amalgam in ethereal solution. Attempts to

effect an internal condensation in the peri-position by the action of dehydrating agents yielded no definite results. When treated with semicarbazide, it yields a substance,  $C_{16}H_{16}ON_2Cl$ , the constitution of which has not yet been determined. F. B.

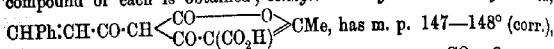
**Labile Isomerides of the Same Structure, which can be Converted One into Another.** EMIL ERLERMAYER (*Biochem. Zeitsch.*, 1911, 24, 306—353).—The author gives the history of the discovery of the various isomerides of cinnamic acid discovered by Liebermann and Erlenmeyer, sen., and of the additions made to the knowledge of these acids by himself and his pupils. He considers that the following labile acids, of which the crystals have been measured, are known to exist, namely: *iso*Cinnamic acid of Erlenmeyer, sen., the *isocinnamic* acid in dextrohemihedral and holohedral forms of Liebermann, hemihedral and holohedral forms of *allocinnamic* acid, and triclincic cinnamic acid. There are, therefore, more isomerides than can be accounted for from the structure and chemical configuration, and the author explains the differences on the assumption of a difference of space disposition in some part of the molecule, the exact character of which is not yet known. He draws the following conclusions from the investigations summarised in this communication. The *iso*-acid as originally described by Erlenmeyer, sen., exists, and possesses the properties originally ascribed to it. It can be changed, however, into the *allo*-acid; it gives with aniline, as Liebermann showed, the aniline salt of the *allo*-acid. The latter acid on treatment with small quantities of an alcoholic solution of zinc bromide is converted into the Erlenmeyer *iso*-acid. The *iso*-acid (E) is also converted into the *allo*-form when left in contact with dilute sulphuric acid. The *iso*-acid of Liebermann prepared from natural sources also exists, and has m. p. 58—59° (from light petroleum); it spontaneously changes into the *allo*-acid, and can be prepared by the reduction of the  $\alpha$ -bromo*allocinnamic* acid. It is an actual modification and not merely a component of the *iso*-acid (L). In addition to existence in nature, it can also be prepared artificially: (a) by making the brucine salt of the *allo*-acid, and (b) by reduction of the  $\alpha$ -bromo*allo*-acid. When the *allo*-acid is neutralised with brucine, two salts can be separated from one another by fractional crystallisation, which differ from one another in solubility, melting point, polarisation, etc. One of these yields the *iso*-acid (L) in hemihedral, and the other the *iso*-acid of holohedral, form. Possibly three brucine salts are formed when the acid is neutralised in this way.

S. B. S.

**Constitution of Dehydracetic Acid.** WILLIAM J. HALE (*J. Amer. Chem. Soc.*, 1911, 33, 1119—1135).—Evidence of a positive and of a negative character is advanced to support Feist's rather than Collie's formula of dehydracetic acid. The negative evidence is based on the fact that sodionitromalonie aldehyde, which reacts very readily with the group  $\cdot CH_2 \cdot CO \cdot CH_2 \cdot$ , does not attack dehydracetic acid. The positive evidence is of two kinds. Firstly, Goldschmidt, Harries, and others have shown that aromatic aldehydes react with saturated asymmetrical ketones in two ways, preferably with the methyl group



adjacent to the carbonyl group in alkaline solution, but with the methylene group in the presence of acid. Dehydracetic acid (and also dehydracetocarboxylic acid), constituted in accordance with Feist's views, allows of the formation of one benzylidene derivative by condensation with benzaldehyde. Collie's formulation of the two acids permits of the possibility of three ways of condensation, and the probability of the formation of two benzylidene compounds in acid solution. The facts are, however, that dehydracetic acid and dehydracetocarboxylic acid do not condense with benzaldehyde in acid solution, whilst in aqueous sodium hydroxide, one benzylidene compound of each is obtained; *benzylidenedehydracetocarboxylic acid*,



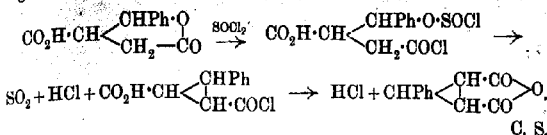
and *benzylidenedehydracetic acid*,  $\text{CHPh}:\text{CH}\cdot\text{CO}\cdot\text{CH} \begin{array}{c} \text{CO} \text{---} \text{O} \\ \text{CO}\cdot\text{CH} \end{array} \text{CMe}$ , has m. p.  $105\text{--}106^\circ$  (corr.), both compounds yielding dehydracetic acid by sublimation.

Further evidence against Collie's formula for dehydracetic acid is obtained by an examination of von Pechmann's synthesis of the acid from acetonedicarboxylic acid and acetic anhydride or acetyl chloride. Both Feist and Collie indicate possible courses of this reaction which lead each to his own constitution of dehydracetic acid. The author shows that acetonedicarboxylic acid, when heated on the water-bath with an excess of benzoic anhydride or benzoyl chloride, yields *s*-*dibenzoylacetonedicarboxylic acid*,  $\text{CO}_2\text{H}\cdot\text{CHBz}\cdot\text{CO}\cdot\text{CHBz}\cdot\text{CO}_2\text{H}$ , m. p.  $162^\circ$  (corr.), which reacts with acetic anhydride and a few drops of concentrated sulphuric acid, yielding dehydracetocarboxylic and benzoic acids, owing to a displacement of the benzoyl by acetyl groups. There is little doubt, therefore, that the initial step in von Pechmann's reaction is the direct interaction of the methylene hydrogen atoms of acetonedicarboxylic acid with the acetic anhydride; Collie's explanation would not permit of a reaction between acetonedicarboxylic acid and benzoic anhydride.

*s*-Dibenzoylacetonedicarboxylic acid contains four ionisable hydrogen atoms, decomposes when heated, and is easily hydrolysed to benzoic and acetonedicarboxylic acids. Its *diethyl ester*,  $\text{C}_{25}\text{H}_{20}\text{O}_7$ , m. p.  $70\cdot5^\circ$  (corr.), contains two ionisable hydrogen atoms, also decomposes when heated, and does not react with acetic anhydride; it is hydrolysed by boiling aqueous barium hydroxide, yielding benzoic and acetonedicarboxylic acids. C. S.

**Conversion of Substituted Paraconic Acids into the Isomeric cycloPropanedicarboxylic Acids.** PHILIPPE BARBIER and RENÉ LOCQUIN (*Compt. rend.*, 1911, 153, 188—191).—Phenylparaconic acid and terebic acid, when their solutions in about one and a-half times the weight of benzene are heated for twelve hours with thionyl chloride on the water-bath, are converted into the anhydrides of *cis*-3-phenylcyclopropane-1:2-dicarboxylic acid and *cis*-3:3-dimethylcyclopropane-1:2-dicarboxylic acid respectively, sulphur dioxide and

hydrogen chloride being evolved. The reaction, which appears to be a general one for lactonic acids, follows probably the course:

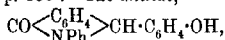


**Spectrographic Studies in the Phthalein Group.** RICHARD MEYER and OTTO FISCHER (*Ber.*, 1911, 44, 1944—1954).—With the object of ascertaining the cause of the difference in colour exhibited by the *p*-hydroxy- and di-*p*-hydroxy-derivatives of triphenylmethane, the authors have examined the ultra-violet absorption spectra of the sodium salts of phenolphthalein, tetrabromophenolphthalein, fluorescein, quinolphthalein, *p*-hydroxyphenylphthalide, and *p*-hydroxydiphenylphthalide in aqueous solution.

It is found that the spectra of the four first-named compounds are all similar in character, and show well-marked absorption bands, which, however, are lacking in the case of the salts of *p*-hydroxyphenylphthalide and *p*-hydroxydiphenylphthalide, but whether these results support the view put forward by Baeyer (*Abstr.*, 1907, i, 754) that the colour of the disubstituted derivatives of triphenylmethane is due to a rhythmic movement in the molecule, whereby each of the two substituted benzene nuclei alternately acquire a quinonoid structure, has not been determined.

The following new derivatives of *p*-hydroxyphenylphthalide and *p*-hydroxydiphenylphthalide are described.

*p*-Benzoyloxyphenylphthalide,  $\text{CO} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{O} \end{array} \text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OBz}$ , crystallises in colourless, rectangular plates, m. p. 188°. *p*-Ethoxyphenylphthalide,  $\text{C}_{18}\text{H}_{14}\text{O}_3$ , prepared by the action of ethyl iodide and alcoholic sodium ethoxide on *p*-hydroxyphenylphthalide, forms rhombic plates, m. p. 116°; the corresponding benzyl ether,  $\text{C}_{21}\text{H}_{16}\text{O}_3$ , crystallises in prismatic needles, m. p. 180°. The anilide,



prepared by heating *p*-hydroxyphenylphthalide with aniline and aniline hydrochloride, forms colourless needles, which become brown at 250° and have m. p. 267°.

*p*-Benzoyloxydiphenylphthalide,  $\text{CO} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{O} \end{array} \text{CPh}\cdot\text{C}_6\text{H}_4\cdot\text{OBz}$ , crystallises in triangular prisms, m. p. 139°.

*p*-Ethoxydiphenylphthalide,  $\text{C}_{22}\text{H}_{18}\text{O}_3$ , forms quadratic plates, m. p. 88°; the methoxy-derivative,  $\text{C}_{21}\text{H}_{16}\text{O}_3$ , prepared by methylating *p*-hydroxydiphenylphthalide with methyl sulphate and potassium hydroxide, crystallises in rectangular prisms, m. p. 86°; the benzyl ether,  $\text{C}_{27}\text{H}_{20}\text{O}_3$ , crystallises from glacial acetic acid in rectangular prisms, m. p. 109°.

The *anilide*,  $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{NPh} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , forms hexagonal plates, m. p. 276°. F. B.

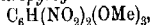
**Action of Nitric Acid on Trimethylgallic [3:4:5-Trimethoxybenzoic] Acid and its Methyl Ester.** Constitution of *Antiarol*. HERMANN THOMS and W. SIEBELING (*Ber.*, 1911, 44, 2115—2125).—When 3:4:5-trimethoxybenzoic acid in glacial acetic acid solution is treated with fuming nitric acid at  $-15^\circ$ , the carboxyl group is displaced by a nitro-group, with the formation of 5-nitropyrogallol trimethyl ether (compare Schiffer, *Abstr.*, 1892, i, 715).

Nitration under similar conditions, but at a higher temperature, results in the formation of 5:6-dinitropyrogallol trimethyl ether, which has m. p.  $119^\circ$ , and not  $126^\circ$ , as given by Will (*Abstr.*, 1888, 457).

The nitration of methyl 3:4:5-trimethoxybenzoate yields either methyl 2-nitro-3:4:5-trimethoxybenzoate or methyl 2:6-dinitro-3:4:5-trimethoxybenzoate, according to the conditions under which the reaction is carried out. The last-named compound, which crystallises in colourless needles, m. p.  $111^\circ$ , is obtained by the gradual addition of fuming nitric acid to a glacial acetic acid solution of the ester, the reaction being completed by warming the mixture.

2-Nitro-3:4:5-trimethoxybenzoic acid, prepared by hydrolysing the corresponding methyl ester with alcoholic potassium hydroxide, crystallises from benzene in colourless prisms, m. p.  $163\text{--}164^\circ$ , which lose carbon dioxide when heated at  $190\text{--}220^\circ$ ; the *silver* and *barium* salts were analysed. When warmed with strong nitric acid the carboxyl group is displaced by the nitro-group with the formation of 5:6-dinitropyrogallol trimethyl ether.

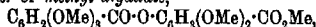
2:6-Dinitro-3:4:5-trimethoxybenzoic acid,  $\text{C}_6(\text{OMe})_3(\text{NO}_2)_2 \cdot \text{CO}_2\text{H}$ , obtained by the hydrolysis of the methyl ester with dilute alcoholic potassium hydroxide at the ordinary temperature, forms colourless needles, m. p.  $158\text{--}160^\circ$ , which become yellow on exposure to light; the *barium* salt crystallises in pale yellow prisms, the *silver* salt in yellow, microscopic needles. When heated at  $194^\circ$ , it loses carbon dioxide, yielding 4:6-dinitropyrogallol trimethyl ether,



which forms large, yellow, transparent crystals, m. p.  $85^\circ$ . On further nitration by means of a mixture of fuming nitric and concentrated sulphuric acids below  $20^\circ$ , it is converted into 4:5:6-trinitropyrogallol trimethyl ether; this crystallises in slender, yellow needles, m. p.  $128^\circ$ .

Reduction of 6-nitropyrogallol trimethyl ether, followed by the displacement of the amino-group by hydroxyl by means of the diazo-reaction, gives rise to 5-hydroxypyrogallol trimethyl ether, m. p.  $146^\circ$ . The latter compound is identical with the phenol first obtained by Will (*loc. cit.*) by the partial methylation of dimethoxyquinol, and subsequently isolated by Kiliani (*Abstr.*, 1897, i, 91) from the sap of *Antiaris toxicata*, under the name of *antiaryl*. F. B.

**Synthesis of Methyl Digallatepentamethyl Ether.** FERDINAND MAUTHNER (*J. pr. Chem.*, 1911, [ii], 84, 140—143).—The 3:4:5:2':6'-pentamethyl ether of methyl digallate,



is formed by shaking an ethereal solution of gallyl chloride trimethyl ether (Perkin and Weizmann, *Trans.*, 1906, 89, 1655) with an aqueous solution of the sodium derivative of methyl syringate (Graebe and Martz, *Abstr.*, 1905, i, 703), and crystallises from a mixture of benzene and light petroleum in needles, m. p. 169—170°. When boiled for ten hours with aqueous alcoholic potassium hydroxide, it yields the trimethyl ether of gallic acid and syringic acid, which can be separated by means of their calcium salts. J. J. S.

**Formation of Benzaldehyde and 2:4:6-Tribromoaniline from 3:5-Dibromo-4-aminobenzhydrol by the Action of Bromine.** LATHAM CLARKE and GUSTAVUS J. ESSELEN, jun. (*J. Amer. Chem. Soc.*, 1911, 33, 1135—1140).—*p*-Aminobenzophenone is conveniently obtained by heating benzoyl chloride (2 mols.) and aniline for fifteen minutes at 170—180°, then adding zinc chloride, and heating again for ten hours at 200—210° (compare Chattaway, *Trans.*, 1904, 85, 394); the resulting *p*-benzoylamino benzophenone is hydrolysed by alcoholic sodium hydroxide.

By treatment with bromine (2 mols.) in dry chloroform, *p*-aminobenzophenone yields 3:5-dibromo-4-aminobenzophenone, m. p. 146°, which is reduced by aluminium amalgam to 3:5-dibromo-4-aminobenzhydrol, m. p. 147.5°. This substance, by bromination (1 mol.) in dry chloroform, is decomposed into benzaldehyde, hydrogen bromide, and 2:4:6-tribromoaniline. The formation of the last compound is the proof of the position of the halogen atoms in 3:5-dibromo-4-aminobenzophenone. C. S.

**Steric Hindrance.** PAVEL IW. PETRENKO-KRITSCHENKO (*J. pr. Chem.*, 1911, [ii], 84, 143—144. Compare *Abstr.*, 1910, i, 177).—It is pointed out that Stewart (this vol., i, 210) admits that steric hindrance affords a simple explanation of the phenomena met with in the study of cyclic ketones and amides. J. J. S.

**The Study of Hydro-aromatic Substances.** EDWARD DIVERS, ARTHUR W. CROSSLEY, WILLIAM H. PERKIN, MARTIN O. FORSTER, and HENRY R. LE SUEUR (*Brit. Assoc. Reports*, 1910, 82—84).—This report deals with the action of ethyl cyanoacetate on 5-chloro-1:1-dimethyl- $\Delta^4$ -cyclohexen-3-one (*Trans.*, 1910, 97, 518) with 3:5-dichloro-*o*-xylene and 3:5-dichlorophthalic acid (*Trans.*, 1910, 97, 98), and also with the preparation of 1:1:2-trimethylcyclohexan-3-one from trimethyldihydroresorcin. T. S. P.

**New Method of Synthesis of Methyl Ketones.** PHILIPPE BARRIER and RÉNÉ LOCQUIN (*Bull. Soc. chim.*, 1911, [iv], 9, 722—726).—In a previous paper (this vol., i, 708), mention was made of a new method of preparing methyl ketones. This has now been worked out as a general method, and it has been applied in particular to the

preparation of benzyl methyl ketone from methyl dimethylacetate and magnesium benzyl chloride. A 40% yield resulted. In general, organo-magnesium compounds of the type  $R \cdot Mg \cdot X$ , by condensation with an ester of the type  $R_1 > C \begin{smallmatrix} CO \cdot CH_3 \\ CO_2 R_2 \end{smallmatrix}$  and subsequent saponification, will yield the ketone  $R \cdot CO \cdot CH_3$ . Condensation with an ester of the type  $CHR_1 \cdot C \begin{smallmatrix} CO \cdot CH_3 \\ CO_2 X \end{smallmatrix}$  yields a branched ketone of the type  $CH_3 \cdot CO \cdot CH_2 \cdot CH \begin{smallmatrix} R \\ R_1 \end{smallmatrix}$ .

W. G.

**Ketones of the Type of  $\alpha$ -Benzyl- $\alpha$ -dimethylacetophenone.** Trialkylacetic Acids and Trialkylmethylcarbinols to which They Give Rise. ALBIN HALLER and EDOUARD BAUER (*Compt. rend.*, 1911, 153, 21—27. Compare Abstr., 1909, i, 654).—The general method already described has been applied to the synthesis of new ketones from phenyl isopropyl ketone. The sodium derivative of this substance treated with *o*-xylyl bromide gives  $\alpha$ -*o*-xylyl- $\alpha$ -dimethylacetophenone,  $COPh \cdot CMe_2 \cdot CH_2 \cdot C_6H_4Me$ , b. p. 199—200°/15 mm.; the *m*-xylyl derivative is an oil, b. p. 196—197°/12 mm., whilst the *p*-xylyl derivative has b. p. 200—202°/13 mm.  $\alpha$ -*p*-Methoxybenzyl- $\alpha$ -dimethylacetophenone,  $COPh \cdot CMe_2 \cdot CH_2 \cdot C_6H_4 \cdot OMe$ , is a viscid liquid, b. p. 222—224°/15 mm.

The new ketones react normally with sodamide, giving rise to the following amides. *o*-Tolyl- $\alpha$ -methylisobutyramide, pearly spangles, m. p. 62—63°, b. p. 188—192° in a vacuum; *o*-tolyl- $\alpha$ -methylisobutyric acid,  $C_7H_7 \cdot CH_2 \cdot CMe_2 \cdot CO_2H$ , has m. p. 48°, b. p. 180—181°/16 mm. *m*-Tolyl- $\alpha$ -methylisobutyramide has m. p. 46—47°, and the *p*-tolyl derivative, m. p. 85—86°; the two corresponding acids have b. p. 178°/16 mm. and m. p. 53—54°, b. p. 180°/16 mm. respectively. *p*-Anisyl- $\alpha$ -methylisobutyramide separates from ether in prisms probably containing ether of crystallisation, m. p. 72°, after resolidification m. p. 99—100°; the acid has m. p. 52—53°.

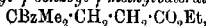
On reduction with sodium and alcohol, *o*-tolyl- $\alpha$ -methylisobutyramide gives an 80% yield of the carbinol,  $C_7H_7 \cdot CH_2 \cdot CMe_2 \cdot CH_2 \cdot OH$ , b. p. 142—143°/15 mm., and a 5—7% yield of *o*-xylyldimethylethylamine,  $C_7H_7 \cdot CH_2 \cdot CMe_2 \cdot CH_2 \cdot NH_2$ , b. p. 129—130°/13 mm.; the platnichloride is crystalline. The corresponding *m*-xylyl-carbinol has b. p. 139—140°/16 mm., and the amine, b. p. 134—135°/15 mm. The *p*-xylyl-carbinol has m. p. 37°, b. p. 141°/15 mm. *p*-Anisyl- $\beta$ -methylisobutyl alcohol,  $C_7H_7 \cdot O \cdot CH_2 \cdot CMe_2 \cdot CH_2 \cdot OH$ , has m. p. 50°.

W. O. W.

**Synthesis of Substituted  $\beta$ -Diketones, Ketonic Esters, and Enolic Esters by means of Ketones and Sodamide.** ALBIN HALLER and EDMOND BAUER (*Compt. rend.*, 1911, 153, 145—152).—The sodium derivative of a ketone,  $R \cdot CO \cdot CHR'_2$ , reacts with acid chlorides as though  $R \cdot CO \cdot CNaR'_2$  and  $R \cdot C(ONa) \cdot CR'_2$  were both present, but with ethyl  $\beta$ -iodopropionate as though only the former is present. Thus phenyl isopropyl ketone, sodamide, and benzoyl chloride yield  $\beta\beta$ -dibenzoylpropane,  $CBz_2Me_2$ , b. p. 195—196°.

15 mm., m. p. 99—100° (*oxime*,  $\text{NOH:CPh}\cdot\text{CBzMe}_3$ , m. p. 166°), and  $\alpha$ -phenyl- $\beta\beta$ -dimethylvinyl benzoate,  $\text{CMe}_3\cdot\text{CPh}\cdot\text{O}\cdot\text{COPh}$ , b. p. 194—196°/13.5 mm., m. p. 53—54°; the latter does not form an *oxime*, and is hydrolysed by cold alcoholic potassium hydroxide or 1% methyl-alcoholic hydrogen chloride, whilst the former is converted into benzoic acid and phenyl isopropyl ketone by boiling alcoholic potassium hydroxide. Similarly, isopropyl *tert*-butyl ketone, sodamide, and benzoyl chloride in benzene yield  $\beta$ -benzoyl- $\beta$ -pivaloylpropane,  $\text{CMe}_3\cdot\text{CO}\cdot\text{CMe}_3\cdot\text{COPh}$ , m. p. 35° (*oxime*, m. p. 178°), and an oil which is shown to contain the benzoate,  $\text{CMe}_3\cdot\text{C}(\text{OBz})\cdot\text{CMe}_3$ . Pivaloyl chloride, isopropyl *tert*-butyl ketone, and sodamide in benzene yield a liquid, b. p. 213—214° or 102°/18 mm., which doubtless is a mixture of  $\beta\beta$ -dipivaloylpropane and the isomeric enolic ester; it does not form an *oxime* or semicarbazone.

Ethyl  $\beta$ -iodopropionate, phenyl isopropyl ketone, and sodamide in ether yield mainly ethyl  $\gamma$ -benzoyl- $\gamma$ -methylvalerate,



b. p. 183°/13 mm. (*oxime*, m. p. 119—120°), which is hydrolysed by potassium hydroxide to the acid, an oil which forms an *oxime*,  $\text{NOH:CPh}\cdot\text{CMe}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p. 123—124°. Under similar conditions ethyl  $\beta$ -iodopropionate and phenyl propyl ketone yield ethyl  $\gamma$ -benzoylhexoate,  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{Et})\cdot\text{Bz}$ , b. p. 189—191°/15 mm. (*p*-nitrophenylhydrazone, yellow crystals, m. p. 205°).

Summarising this and Claisen's work, it is seen that with the sodium derivatives of ketones: (1) acid chlorides and ethyl chloroformate yield isomeric C and O derivatives; (2) ethyl chloro- or bromo-acetate yields glycidic esters; (3) ethyl  $\beta$ -iodopropionate, like the alkyl halides, reacts normally and yields  $\delta$ -ketonic esters. C. S.

**Explanation of the Reaction between *p*-Benzoquinone and Hydrogen Chloride.** JULIUS SCHMIDLIN (*Ber.*, 1911, 44, 1700—1705. Compare Posner, *Abstr.*, 1904, i, 1029; 1909, i, 809; Michael, *Abstr.*, 1904, ii, 164; 1909, i, 494; 1910, i, 748).—The author draws attention to the equilibrium which exists between *p*-benzoquinone and chloroquinol on the one hand, and chloro-*p*-benzoquinone and quinol on the other:  $\text{O:C}_6\text{H}_4\text{:O} + \text{C}_6\text{H}_5\text{Cl(OH)}_2 \rightleftharpoons \text{O:C}_6\text{H}_4\text{Cl:O} + \text{C}_6\text{H}_4\text{(OH)}_2$ .

In the reaction between hydrogen chloride and quinone the conclusion is drawn that the quinone combines with hydrogen chloride, and that the resulting chloroquinol reacts with the quinone, yielding chloro-*p*-benzoquinone and quinol. The equilibrium is disturbed by the separation of quinol in the form of the sparingly soluble quinhydrone, and thus all the free *p*-benzoquinone is transformed into chloro-*p*-benzoquinone and quinhydrone. A subsidiary reaction is that of hydrogen chloride on the quinone present in the form of quinhydrone, the formation of chloroquinol and quinol, and the reaction between the quinol and chloro-*p*-benzoquinone, resulting in the formation of *p*-benzoquinone and chloroquinol.

Hydrogen bromide behaves in a somewhat similar manner, except that the bromo-*p*-benzoquinone can react with hydrogen bromide, forming dibromoquinol.

When saturated solutions of *p*-benzoquinone and chloroquinol or of

chloro-*p*-benzoquinone and quinol are mixed, the precipitate formed consists of nearly pure quinhydrone. The best solvent for the first pair of compounds is water, and for the second pair ether or chloroform.

These results confirm the conclusion drawn by Wichelhaus (Abstr., 1880, 42) that it is impossible to obtain a pure chloroquinhydrone by bringing together quinone and a chlorinated quinol. The products described by Ling and Baker (Trans., 1893, 63, 1314) are mixtures.

When *p*-benzoquinone and chloroquinol are brought together in benzene solution, a chloroquinhydrone is first formed, but when this is heated with the benzene for some time, reaction takes place, and the non-chlorinated quinhydrone is formed on cooling.

Chloro-*p*-benzoquinone has a pale lemon-yellow, and not a yellowish-red, colour. J. J. S.

**Quinonoid Compounds. XXVI. *o*-Quinones.** RICHARD WILL-STÄTTER and FRITZ MÜLLER (*Ber.*, 1911, 44, 2171—2181. Compare Abstr., 1908, i, 731).—The following substances have been prepared in the hope of throwing some light on the conditions of equilibrium of the two desmotropic forms of *o*-benzoquinones. The method is that used previously (*loc. cit.*)—rapid oxidation of the corresponding catechol in dry ether by dry silver oxide in the presence of anhydrous sodium sulphate. All of the quinones form stable, deep red crystals, the colourless form being observed only in the case of homo-*o*-benzoquinone; frequently, however, the product of oxidation is obtained in yellow crystals, which are probably mixtures of the red and the colourless modifications. The red forms are shown to be unimolecular. The instability of the colourless forms negatives the suggestion that they may be polymerides; moreover, since they give the reactions of quinones, whilst the bimolecular forms described below do not, it is justifiable to assume that the colourless forms also are unimolecular.

The oxidation of homocatechol under the stated conditions yields *homo-o*-benzoquinone [*3:4-toluquinone*],  $\text{O}:\text{C}_6\text{H}_3\text{Me}:\text{O}$ . Only occasionally, by treating the freshly oxidised solution with petroleum and cooling rapidly in a freezing mixture, have colourless crystals been observed. Usually, by rapid evaporation of the solvent, yellow (mixed) crystals, m. p. 65—67°, are obtained; by recrystallisation they yield the deep red form, m. p. 80—84°, which is more stable than *o*-benzoquinone itself. The substance is readily reduced by cold saturated sulphurous acid. When exposed to sunlight or warmed in ether or acetone, it changes to a *bimolecular* form,  $(\text{C}_6\text{H}_3\text{O}_2)_2$ , yellow, rhombic prisms, m. p. 124—125°, which has not been depolymerised.

*isoHomo-o*-benzoquinone [*2:3-toluquinone*], prepared from 2:3-dihydroxytoluene, forms unstable dark red prisms and needles, and polymerises, by warming or keeping its ethereal solution, to the *bimolecular* form, m. p. 194—195°, yellow, monoclinic prisms and plates. 3-Methoxy-1:2-benzoquinone,  $\text{O}:\text{C}_6\text{H}_3(\text{OMe}):\text{O}$ , m. p. 115—120°, obtained from pyrogallol 1-methyl ether, forms dark red crystals; the *stability* is such that its solutions in alcohol, water, or dilute sulphuric acid exhibit the reactions of *o*-quinones.

The oxidation of hydroxyquinol by silver oxide yields a quinone which is shown to be *hydroxy-p-benzoquinone* by its yellow colour, stability, tendency to form a *quinhydrone* (greenish-black prisms), similarity to the long-known methoxy-*p*-benzoquinone, and difference from 3-methoxy-*o*-benzoquinone. It darkens at 120—124°, and is easily reduced to hydroxyquinol. C. S.

**Quinonoid Compounds. XXVII. Chloro-derivatives of Catechol and of *o*-Benzoquinone.** RICHARD WILLSTÄTTER and HANS EDUARD MÜLLER (*Ber.*, 1911, 44, 2182—2191).—Peratoner states that the chlorination of phenols by sulphuryl chloride yields only para-substituted derivatives; with catechol in ether, however, the authors get about 1% of the ortho-isomeride, which is separated by its greater solubility in benzene and its lower b. p. Pure *p*-chlorocatechol has b. p. 136—136·5°/8·5 mm., and a double m. p. It melts at 90—91°; after resolidification, it melts at 59—61°, again becomes solid, and then has m. p. 90° again. The *diacetate* has b. p. 145—147°/7·5 mm., and the *dibenzoate* has m. p. 96—97°. *o*-Chlorocatechol has b. p. 110—111°/11 mm., and m. p. 46—48°; its *dibenzoate* has m. p. 108—109°. 4:5-Dichlorocatechol has m. p. 116—117° (Peratoner and Vitali give 105—106°), and forms a *dibenzoate*, m. p. 140—140·5°. By treating an alcoholic solution of tetrachlorocatechol with water, a *trihydrate*,  $C_6Cl_3(OH)_3 \cdot 3H_2O$ , m. p. 94°, is obtained. *o*-Benzoquinone is rapidly dissolved and decolorised by 2% ethereal hydrogen chloride, yielding a mixture of *o*- and *p*-chlorocatechols. 4-Chloro-*o*-benzoquinone, m. p. 78° (decomp.), is obtained from *p*-chlorocatechol by the silver oxide method, and crystallises in red needles, which cannot be kept long without decomposing. 3-Chloro-*o*-benzoquinone, obtained by oxidising *o*-chlorocatechol with silver oxide or lead peroxide, forms red prisms, which decompose at about 68°. 4:5-Dichloro-*o*-benzoquinone, yellow or yellowish-red prisms and plates, m. p. 94° (decomp.), is considerably more stable than the monochlorobenzoquinones. It forms a *quinhydrone*,  $C_{12}H_6O_4Cl_2$ , glistening, black prisms, decomp. 85°, with the corresponding catechol. The monochloro- and non-halogenated *o*-benzoquinones do not form quinhydrones. C. S.

**A New Method for Obtaining Acenaphthenequinone from Acenaphthene.** ARNOLD REISSERT (*Ber.*, 1911, 44, 1749—1752).—A mixture of two isomeric acenaphthenequinone monoximes (annexed constitution) is formed when amyl nitrite (4 mols.) is added to a boiling amyl-alcoholic solution of acenaphthene while a stream of hydrogen chloride is passed through the solution. The amyl alcohol is removed by steam distillation, the oximes extracted with sodium hydroxide solution, and separated by means of their different degrees of acidity. The one oxime is insoluble in hot sodium carbonate solution, and crystallises from glacial acetic acid in soft, faintly yellow crystals, m. p. 207° (decomp.). When the oxime is boiled for some time with glacial acid it yields the isomeric oxime (Francesconi and Pirazzoli, *Abstr.*, 1903, i, 500), which has





m. p.  $220^{\circ}$ , but then solidifies, and again melts at  $280-300^{\circ}$ . The quinone can be obtained by hydrolysing the monoxime with 75% sulphuric acid at  $100^{\circ}$ . J. J. S.

**The Catalysis of Borneol and the Catalytic Hydrogenation of Camphor.** JULES ALOY and V. BRUSTIER (*Bull. Soc. chim.*, 1911, [iv], 9, 733-735).—The authors have employed the method of Sabatier and Senderens (*Abstr.*, 1905, i, 401) in transforming borneol into camphor. The three metals nickel, iron, and copper have been tried, copper being the best. The optimum temperature is  $300^{\circ}$ , when the yield is theoretical. Above this temperature, terpene-like products are formed.

The hydrogenation of camphor in the presence of reduced nickel was not successful, but in the presence of this metal, camphoroxime was readily transformed into amines, the secondary amine predominating. W. G.

**Hydrogenation of Carvone.** GUSTAVE VAYON (*Compt. rend.*, 1911, 153, 68-71. Compare this vol. i, 657).—The reduction of carvone at the ordinary temperature by hydrogen in presence of platinum-black takes place in three stages, corresponding with the formation of carvotanacetone, tetrahydrocarvone, and carvomenthol. This furnishes the most convenient method for preparing *d*-carvotanacetone; the product has b. p.  $227-228^{\circ}$ ,  $D_4^{20}$  0.937,  $n_D^{20}$  1.4817,  $[\alpha]_D^{20}$   $59.8^{\circ}$ . The final stage of the reduction takes place with greater difficulty. W. O. W.

**Specific Rotatory Power of Camphor in Acetone Solution.** H. MALOSSE (*Compt. rend.*, 1911, 153, 56-57).—The specific rotation of camphor in acetone at different temperatures and concentrations is shown in a tabular statement. The results have been plotted in the form of a curve, and the equations to the different parts of the curve calculated. W. O. W.

**The Isomeric Tanacetyl Alcohols.** VINCENZO PAOLINI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 765-769).—By recrystallisation of the hydrogen phthalates of the mixture of alcohols obtained by reduction of tanacetone from the natural oil, and subsequent saponification, the author has isolated a pure *d*-tanacetyl alcohol, and has obtained indications of the presence of the corresponding *l*-compound in the mother liquor. R. V. S.

**Some Derivatives of *d*-Tanacetyl Alcohol.** VINCENZO PAOLINI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 769-772).—The tanacetyl alcohol employed had b. p.  $206-209^{\circ}$ ,  $D_4^{20}$  0.925,  $n_D^{20}$  1.4635,  $[\alpha]_D^{20}$   $69.49^{\circ}$ . This was dissolved in light petroleum and treated with sodium, and the sodium derivative produced was added to the calculated quantity of phthalic anhydride in light petroleum. The product is a mixture of several esters, from which by repeated crystallisation a pure *tanacetyl hydrogen phthalate*,  $C_{18}H_{22}O_4$ , was obtained in tufts of colourless needles, m. p.  $120^{\circ}$ ,  $[\alpha]_D^{20}$   $+91.27^{\circ}$ . Its silver salt,  $C_{18}H_{21}O_4Ag$ , has m. p.  $85-86^{\circ}$ . The calcium salt,  $(C_{18}H_{21}O_4)_2Ca$ , was also prepared.

The *strychnine* salt,  $C_{18}H_{21}O_4C_{21}H_{22}O_2N_2$ , has m. p.  $177-178^\circ$ ,  $[\alpha]_D^{25} 36.78^\circ$ .

When the phthalate is saponified with alcoholic potassium hydroxide, *d-tanacetyl alcohol* ( $\beta$ -thujyl alcohol) is obtained. It is an oily liquid, b. p.  $206^\circ$ ,  $D_{20} 0.9229$ ,  $n_D^{20} 1.4625$ ,  $[\alpha]_D^{20} 114.67^\circ$ . When treated with sodium and phthalic anhydride it regenerates the above-mentioned phthalate, and if it is oxidised with chromic acid it yields a ketone, the semicarbazone of which has all the properties of Wallach's  $\beta$ -tanacetonesemicarbazone (Abstr., 1905, i, 147). R. V. S.

**Isoprene from Terpene Hydrocarbons.** HERMANN STAUDINGER and HELMUT W. KLEVER (*Ber.*, 1911, 44, 2212-2215).—By passing the vapour of turpentine through an iron tube at a dark red heat, Tilden obtained a small yield of isoprene, the chief products being hydrocarbons of high b. p. (*Trans.*, 1879, 46, 417). The yield of isoprene is materially increased by working under diminished pressure, but it can be obtained in 60% yield by passing the vapour of dipentene or limonene, under 20-30 mm. or better still 2-3 mm., over an electrically heated platinum spiral. The isoprene thus obtained is almost pure, and contains very little trimethylethylene; the by-products are gaseous substances (olefines and acetylenes) and hydrocarbons, b. p.  $100-150^\circ$ . Terpinolene, terpinene, and camphene give little or no isoprene under these conditions. C. S.

**isocamphane.** PETER LIPP (*Annalen*, 1911, 382, 265-305).—Camphene has been reduced under varying conditions, and the saturated, bicyclic hydrocarbons,  $C_{10}H_{18}$ , obtained were oxidised in different ways. The symmetrical, saturated cyclic hydrocarbon corresponding with bornylene should be termed bornylene, but as the name camphane has been generally used in chemical literature for this compound, the term is retained and the unsymmetrical, saturated isomeride is termed *isocamphane* (compare Semmler, *Die Aetherische Oele*, 1906, ii, 62).

Technical camphene obtained from pinene hydrochloride was purified by distillation, and the middle fraction, b. p.  $155.5-157^\circ/723$  mm., after four crystallisations from aqueous alcohol had m. p.  $45^\circ$  and  $[\alpha]_D^{25} -18.94^\circ$ . The hydrocarbon was not affected when treated with sodium and boiling ethyl alcohol, but was reduced by Sabatier and Senderens' method, using finely-divided nickel distributed over a pumice surface and kept at  $170-190^\circ$ . After a mixture of hydrogen and the vapour of the hydrocarbon had been passed through the tube three times, the product did not decolorise a chloroform solution of bromine. The product consisted of a mixture of an oily and a solid hydrocarbon. The liquid *isocamphane* is formed in small quantities only, and is probably the reduction product of an impurity (Aschan's pinolene) present in the camphene, as it does not appear to be formed when pure camphene, prepared from isoborneol, is used. It has b. p.  $160-162^\circ$ ,  $[\alpha]_D^{25} +1.15^\circ$  in 10% methyl-alcoholic solution,  $D_{20}^{20} 0.8524$ , and  $n_D^{20} 1.45733$ . The solid isomeride crystallises from methyl alcohol in fern-like masses resembling camphene or ammonium chloride; it has m. p.  $65-67^\circ$  after repeated crystallisation, and is practically inactive. A specimen obtained from pure camphene from

isborneol had m. p. 61.5—63°. The reduction of inactive camphene by Fokin's method (*Zeitsch. angew. Chem.*, 1909, 22, 1496) in ethereal solution and in presence of platinum sponge gave a product with b. p. 164°/713 mm. and m. p. 63—64.5° (corr.). A specimen of *l*-camphene with  $[\alpha]_D^{20} = -80.7^\circ$  and m. p. 44—44.5° when reduced in a similar manner had b. p. 166—166.5° (corr.)/750 mm. and m. p. 62—63° (corr.) after five crystallisations. The solid *isocamphane* has the consistency of paraffin wax, and in appearance closely resembles camphene; its odour is not quite so pronounced, and it is extremely volatile even at the ordinary temperature. It forms an exception to the generalisation that a saturated compound has a lower b. p. than its unsaturated analogue. It has  $D_4^{20}$  0.82757,  $n_D^{20}$  1.43982,  $n_D^{25}$  1.44186, and  $n_D^{30}$  1.45239 at 67°.

Attempts made to reduce *isocamphane* by means of hydriodic acid and iodine under pressure were unsuccessful; after five hours at 240—250° an isomeric hydrocarbon,  $C_{10}H_{18}$ , with b. p. 157.5—160.5°,  $D_4^{20}$  0.8344, was obtained, but this was not homogeneous.

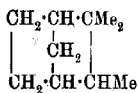
The contradictory statements of Zelinsky (*J. Russ. Phys. Chem. Soc.*, 1904, 38, 768) and Sabatier and Senderens (Abstr., 1901, i, 159; compare Henderson and Pollock, Trans., 1910, 97, 1620) are probably due to the fact that Sabatier and Senderens used an impure specimen of camphene and obtained on reduction a solution of solid *isocamphane* in the liquid isomeride.

Contrary to Sabatier's statement, *isocamphane* is comparatively stable towards oxidising agents. It is most readily oxidised by adding powdered permanganate to a warm 50% acetic acid solution of the hydrocarbon. Among the products are unaltered hydrocarbon (60%), a product containing oxygen and with an odour of camphor, a mixture of camphenilone and camphenilaldehyde, together with camphenilanic acid and *isocamphenilanic acid* (Bredt and Jagelki, Abstr., 1900, i, 134). A mixture of the calcium salts of the two acids is less soluble in hot than in cold water, although each salt independently is more soluble. *Camphenilaldehydesemicarbazone*,  $C_{11}H_{19}ON_2$ , crystallises from dilute alcohol in colourless plates, m. p. 200° (decomp.).

When *isocamphane* is oxidised with nitric acid ( $D$  1.4) for 8.5 hours at 100° under pressure, the products are camphene nitrosite, camphenil nitrite, and camphenilone (compare Jagelki, Abstr., 1899, i, 627), together with resinous compounds.

When the hydrocarbon is boiled for twelve hours with the nitric acid the same products are obtained, and in addition *isocamphoronic acid* and *carboxyapocamphoric acid* (camphoric acid: Marsh and Gardner, Trans., 1896, 69, 74). The normal ammonium salt of the latter acid has m. p. 213—214° (decomp.) (Marsh and Gardner, 198—199°).

The formation of camphenilanic acid and its isomeride indicates that *isocamphane* and camphene have the same ring system, and the annexed structural formula is accepted. The formation of camphoric acid from this hydrocarbon must be accompanied by molecular rearrangement.



The high m. p. for isocamphane observed by Vavon (Abstr., 1910, i, 52) is probably due to the presence of camphane. J. J. S.

**Constituents of Ethereal Oils. I. Identity of the Aliphatic Terpene from Oil of Hops with Myrcene. II. Methyl Esters of Dicarboxylic Acids. III. Preparation of isobornylformate.** FRIEDRICH W. SEMMLER and ERWIN W. MATER (Ber., 1911, 44, 2009—2012).—I. Chapman (Trans., 1903, 83, 505) has suggested the identity of the aliphatic terpene,  $C_{10}H_{16}$ , from oil of hops with myrcene. A colourless, mobile, almost odourless oil is now obtained from oil of hops, b. p. 62–63°/17 mm.,  $D^{20}_D$  0.7937,  $n_D$  1.4716. On reduction, a compound identical with dihydromyrcene is obtained, characterised by the crystalline tetrabromide, m. p. 87°. On heating with sulphuric and acetic acids, myrcenol,  $C_{10}H_{18}O$ , is formed from the hop oil terpene.

II. *Methyl isofenchonecarboxylate*,  $C_{12}H_{20}O_4$ , has b. p. 131–132°/14 mm.,  $D^{20}_D$  1.0515,  $n_D$  1.4540.

*Methyl camphorate* has b. p. 137–139°/14 mm. (Brühl and Braunschweig give 155°/15 mm.).

*Methyl  $\alpha$ -tanacetogencarboxylate*,  $C_{12}H_{20}O_4$ , has b. p. 129–130°/15.5 mm.,  $D^{20}_D$  1.0525,  $n_D$  1.451.

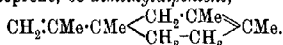
*Methyl  $\beta$ -methyladipate* has b. p. 122–122.5°/18 mm.,  $D^{20}_D$  1.0372,  $n_D$  1.4336.

III. Camphene when boiled with formic acid yields isobornylformate,  $C_{11}H_{20}O_2$ , b. p. 91–93°/11 mm.,  $D^{20}_D$  1.005,  $n_D$  1.4726.

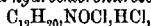
E. F. A.

**Dimethyldipentene Produced by the Dry Distillation of Dimethylcaoutchouc.** A. H. RICHARD (Compt. rend., 1911, 153, 116–120).—Couturier's  $\beta\gamma$ -dimethyl- $\Delta^{\alpha\gamma}$ -butadiene behaves, during its polymerisation, exactly like its lower homologue, isoprene. When submitted to the prolonged action of diffused light, it changes into a viscous, bimolecular form, and finally into a white mass having, in physical and chemical properties, a close resemblance to natural rubber. When polymerised by heating at about 150° for some thirty hours, dimethylbutadiene is converted into a viscous liquid, which is separated by distillation with steam into unchanged hydrocarbon and the polymerised product, homocaoutchouc; however long the heating, the reaction seems to be reversible.

By dry distillation, homocaoutchouc yields: (i)  $\beta\gamma$ -dimethyl- $\Delta^{\alpha\gamma}$ -butadiene, b. p. 69–70°; (ii) a *sesquihomoterpene*,  $C_{18}H_{30}$ , b. p. 175–180°/22 mm.,  $D^{20}_D$  0.912; (iii) polyhomoterpenes of higher b. p.; (iv) a *homoterpene*,  $C_{12}H_{20}$ , b. p. 205° or 97–98°/22 mm.,  $D^{20}_D$  0.872. The last hydrocarbon should, from analogy to the production of dipentene from isoprene, be *dimethyldipentene*,

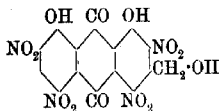


Its molecular refraction, calculated from  $D^{25}_D$  0.85322 and  $n_D$  1.47786, agrees well with the formula  $C_{12}H_{20}$ . The substance forms a viscous *tetrabromide* and a *hydrochloronitroschloride*,



a yellow powder, decomp.  $100^\circ$ , and by reduction with hydrogen and platinum-black yields a hydrocarbon,  $C_{12}H_{22}$ , b. p.  $93-95^\circ/20$  mm.,  $D_4^{20}$  0.842307, and  $n_D^{20}$  1.46635. C. S.

**Constitution of Nitro-compounds Obtained by the Action of Nitric Acid on Aloins.** EUGÈNE LÉGER (*Compt. rend.*, 1911, 153, 114-116).—The author has shown previously that barbaloin and isobarbaloin are converted by nitric acid into a tetranitroalcoemodin, which yields chrysammic acid and 2:4:6-trinitro-*m*-hydroxybenzoic acid by further treatment with nitric acid. Experiments are described now to prove that the trinitro-*m*-hydroxybenzoic acid is formed, not independently of the tetranitroalcoemodin, but at the expense of some of the chrysammic acid. Assuming that Robinson and Simonson's constitution (*Trans.*, 1909, 95, 1088) of the latter is correct, and remembering that the majority of the compounds obtained from the aloins are derivatives of  $\beta$ -methylantraquinone, it follows that tetranitroalcoemodin must be represented by the annexed constitution. Since the aloins are glucosides of alcoemodin and *d*-arabinose, the author is of opinion that the arabinose molecule is attached to the phenolic hydroxyl group in position 1 in barbaloin, and to the phenolic hydroxyl group in position 8 in isobarbaloin. C. S.



**Glucosides from the Leaves of Digitalis purpurea.** F. KRAFT (*Schweiz. Wochensh. Chem. Pharm.*, 1911, Nos. 12, 13, 17; Reprint, 9 pp.).—*Gitalin*, m. p.  $150-155^\circ$ , obtained from the cold aqueous extract of *Digitalis* leaves by means of chloroform, is a white, amorphous glucoside of neutral reaction, which is soluble in 600 parts of cold water. It is soluble in most of the usual solvents, but the solutions decompose more or less quickly. By the addition of water to its alcoholic solution, the glucoside is converted into crystalline *gitalin hydrate*, m. p.  $75^\circ$ , which is soluble in about 3000 parts of water. The decomposition of *gitalin* in solution is accomplished best by the evaporation of an alcoholic solution in a vacuum, whereby *anhydrogitalin*, m. p.  $255^\circ$ , a crystalline glucoside quite insoluble in water, is obtained. Anhydrogitalin is hydrolysed by alcohol and 10% hydrochloric acid on the water-bath, yielding *anhydrogitaligenin*, m. p.  $119^\circ$  (which closely resembles anhydrodigitoxigenin), and two sugars, Kiliani's digitoxose and another, which is not crystallisable.

The literature of digitoxin is very confused. The digitoxin obtained by Keller is claimed by Burmann to be identical with his  $\psi$ -digitoxin (which appears to be identical with *gitalin*). This cannot be so, because Keller's digitoxin is insoluble in water. The author states that *gitalin*, in the form of its hydrate or of anhydrogitalin, is the chief constituent, not only of Keller's, but of all commercial, digitoxins.

*Digitalinum verum* was obtained by Kiliani from the seeds of *Digitalinum germanicum*; it is also present in minute amount in the leaves.

Confusion has also arisen in the literature from the fact that the

name digitonin is given to two substances, Schmiedeberg's amorphous glucoside, and Kiliani's crystalline inactive glucoside. The author retains the name for the latter, and calls the former digitsaponin. From the dilute alcoholic extract of digitalis leaves he obtained an inactive glucoside, m. p. 265° (decomp.), which he regarded at first as identical with digitonin; a direct comparison of the two substances, however, shows that they differ in many important properties. By hydrolysis digitsaponin yields amorphous sapogenins and two sugars, one of which is a pentose, the other dextrose. C. S.

Phloridzin- and Phloretin-glycuronic Acids. JOS. SCHÜLLER (*Zeitsch. Biol.*, 1911, 38, 274—308).—See this vol., ii, 814.

Action of Light of Mercury Lamp on Solutions of Chlorophyll. HENRI BERRY and J. LARGUIER DES BANCELS (*Compt. rend.*, 1911, 153, 124—125).—Alcoholic solutions of chlorophyll (from spinach) in quartz vessels are exposed to the light of two mercury vapour lamps for twenty-four to forty-eight hours. The solutions become faintly yellow, and no longer show the absorption bands characteristic of chlorophyll. Tests for urobilinogen were applied, with positive results. A benzene solution of chlorophyll becomes colourless under the same conditions, but does not show the colour reactions of urobilinogen. C. S.

Chemical Nature of *allo*-Chlorophyll. LEON MARCHLEWSKI and J. MARZALEK (*Ber.*, 1911, 44, 1705—1708. Compare Malarski and Marchlewski, *Abstr.*, 1910, i, 692).—*allo*-Chlorophyllan can be obtained in appreciable amounts from maple leaves: thus, 20 grams of crude chlorophyllan gave 5.76 grams of the *allo*-compound. The compound contains 3% of methoxyl, and prolonged treatment with zinc hydroxide tends to diminish the percentage; it also yields 31.8% of phytol, and when heated at 105° its properties change. The *allo*-chlorophyllanic acids, obtained by hydrolysing the product dried at 105°, are insoluble in ether. The acids have a cherry-red colour, whilst chlorophyllanic acids are olive-green.

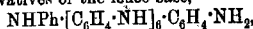
With zinc acetate, *allo*-chlorophyllan yields a zinc derivative, zinc *allo*-chlorophyll, similar to zinc chlorophyll, but with a different absorption spectrum. It is questionable whether *allo*-chlorophyll yields phylloporphyrin, but it is suggested that it contains two carboxyl groups, one present as methyl, and the other as phytyl, ester.

J. J. S.

The Chlorophyll Group. X. Phyllohæmin. II. LEON MARCHLEWSKI and J. ROBEL (*Biochem. Zeitsch.*, 1911, 34, 275—279).—Phyllohæmin was prepared by treatment of phylloporphyrin in warm acetic acid saturated with sodium chloride with permanganate. The substance which separated, after washing free from excess of sodium chloride and iron salt, was recrystallised by Schalféeff's method, that is, by dissolving in chloroform containing quinine, throwing the solution into acetic acid saturated with sodium chloride and kept at 90°, and allowing the mixture to cool. The measurement

of the spectral bands and other properties showed a marked similarity between this preparation and the blood-hæmin. S. B. S.

**Quinonoid Compounds. XXV. Aniline Black. V. RICHARD WILLSTÄTTER and CARL CRAMER** (*Ber.*, 1911, 44, 2162—2171. Compare Abstr., 1909, i, 535, 975).—A criticism of Green and Woodhead's paper (*Trans.*, 1910, 97, 2388). These authors agree with Willstätter and Dorogi (*loc. cit.*) that the oxidation products of aniline are derivatives of the leuco-base,



but dispute most of their other statements. The chief cause of Green and Woodhead's diverging views which the authors consider erroneous, is the fact that the substance which they have regarded as the leuco-base,  $\text{C}_{48}\text{H}_{40}\text{N}_8$ , and have obtained by reducing emeraldine with titanium trichloride, is in reality the monoquinonoid black,  $\text{C}_{48}\text{H}_{40}\text{N}_8$ . The real facts are as follows: Monoquinonoid black,  $\text{C}_{48}\text{H}_{40}\text{N}_8$ , is obtained by reducing triquinonoid black (emeraldine) with titanium trichloride in the cold, or, better, with phenylhydrazine at 100°. Diquinonoid black,  $\text{C}_{48}\text{H}_{38}\text{N}_8$ , is easily obtained pure by the spontaneous oxidation of monoquinonoid black or of the leuco-base in the air. Triquinonoid black (emeraldine),  $\text{C}_{48}\text{H}_{36}\text{N}_8$ , is obtained by oxidising an excess of aniline salt with dichromate, persulphate, chlorate, or other agents. Tetraquinonoid black (nigraniline),  $\text{C}_{48}\text{H}_{34}\text{N}_8$ , is obtained best by oxidising triquinonoid black with hydrogen peroxide. (By oxidation with dichromate or persulphate, an oxygenated pentaquinonoid black,  $\text{C}_{48}\text{H}_{32}\text{ON}_8$ , stable to sulphurous acid, is obtained.) All these quinonoid blacks yield the first-mentioned monoquinonoid black by oxidation by Knecht's titanium trichloride process, in the cold or at 90°. The true leuco-base,  $\text{C}_{48}\text{H}_{42}\text{N}_8$ , is obtained by treating any of these blacks with phenylhydrazine at 150°. (A black which contains iron in its ash must be first boiled with 2*N*-sulphuric acid, otherwise the reaction with phenylhydrazine above 100° proceeds explosively.)

Green and Woodhead state that the salts of nigraniline are very unstable, changing slowly in the cold, rapidly by warming, to emeraldine and *p*-benzoquinone. On the contrary, the authors find that the only change produced by 17% sulphuric acid at 200° is the quantitative hydrolysis of one quinonimine group.

Green and Woodhead also state that the emeraldine and nigraniline dissolve easily and completely in 80% acetic acid or in 60% formic acid. This, again, is incorrect; only suspensions are obtained.

C. S.

**Action of Oxidising Agents on isoPyromucic Acid. Dialdehydes of Dibromomaleic and Bromohydroxymaleic Acids.** G. CHAVANNE (*Compt. rend.*, 1911, 153, 185—188\*).—The constitution of isopyromucic acid previously determined by the author (Abstr., 1905, i, 77), and confirmed by Blaise and Gault (Abstr., 1909, i, 134), is supported by a study of the products of oxidation. Most oxidising agents act too energetically, but hydrogen peroxide in

\* and *Bull. Soc. chim. Belg.*, 1911, 25, 264—279.

alkaline solution at the ordinary temperature produces maleic acid, carbon dioxide, and a little formic acid.

It has been shown (*loc. cit.*) that the action of bromine and water on isopyromucic acid yields, under apparently identical conditions, either a substance,  $C_6H_4O_2Br_2$ , decomp.  $104-105^\circ$ , or a substance,  $C_6H_3O_2Br_2$ , m. p.  $34^\circ$ . These substances can now be obtained at will. *iso*Bromopyromucic acid forms with bromine an additive compound,  $C_6H_3O_2Br_2$ , large prisms, m. p.  $88-89^\circ$ , which is decomposed by ice water, yielding hydrogen bromide and the substance  $C_6H_4O_2Br_2$ , previously described (it decomposes at  $175^\circ$  when pure). All attempts to obtain the substance  $C_4H_2O_2Br_2$  from the substance  $C_6H_4O_2Br_2$  have failed. However, by dissolving the additive compound  $C_6H_3O_2Br_2$  in bromine (1 mol.) and adding the solution to a little water at the ordinary temperature, the substance  $C_6H_3O_2Br_2$ , m. p.  $34^\circ$ , is obtained in good yield. There is no doubt that it is dibromomaleic dialdehyde, because: (i) by oxidation with bromine and water under suitable conditions it gives an almost theoretical yield of bromomucic acid, and (ii) when heated with a large excess of water it decomposes into hydrogen bromide and a substance,  $C_4H_2O_2Br$ , m. p.  $83-83.5^\circ$ , which has acidic properties, forms an *acetyl* derivative, b. p.  $118-120^\circ/1.5$  mm., *semicarbazone*, decomp.  $198^\circ$ , *phenylhydrazone*, decomp.  $126-126.5^\circ$ , and *trioxime*, decomp.  $94-95^\circ$ , reduces ammoniacal silver nitrate, gives Schiff's test, and is oxidised by bromine and water chiefly to bromomucic acid. The substance, therefore, is  $\alpha$ -bromo- $\beta$ -hydroxymaleic dialdehyde, which reacts in the tautomeric forms:  $CHO \cdot C(OH) : CBr \cdot CHO$  and  $CHO \cdot CO \cdot CHBr \cdot CHO$ .  
C. S.

**Action of Halogen Acids on Hydroxyarylxanthenols.**  
MOSES GOMBERG and C. J. WEST (*J. Amer. Chem. Soc.*, 1911, 33, 1211-1213).—Many investigators have examined the action of acids on hydroxyarylxanthenols, and report generally that coloured oxonium salts are formed. The authors have made a systematic study of the reaction (as an introduction to the study of the constitutions of fluoran, fluorescein, etc.), and find that, in general, hydroxy- and methoxy-xanthenols yield colourless carbinol chlorides, which tautomerise with extreme readiness to coloured quinocarbonium salts in the presence of excess of acid (compare Gomberg and Cone, *Abstr.*, 1910, i, 55, 869). When one of the two phenyl groups in the xanthone ring contains a hydroxyl group in the para-position to the carbinol carbon atom, the colourless carbinol halide changes spontaneously, even in the absence of excess of acid, to the coloured quinocarbonium salt. Full information is promised in a later paper.  
C. S.

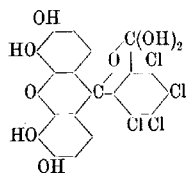
**Tetrachlorogallein and Some of its Derivatives. II.**  
WILLIAM R. ORNDORFF and T. G. DELBRIDGE (*Amer. Chem. J.*, 1911, 43, 1-55. Compare *Abstr.*, 1909, i, 733).—A more convenient method of preparing the coloured tetrachlorogallein hydrate is described, in which tetrachlorophthalic acid, pyrogallol, and zinc chloride are heated at  $200^\circ$  in a current of carbon dioxide.

The authors have extended their investigations of the coloured

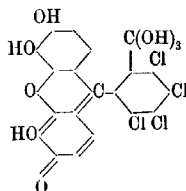


and the colourless derivatives of tetrachlorogallein by the isolation of a colourless tetrachlorogallein hydrate, a colourless tetrachlorogalleincarbinolcarboxylic acid, and two colourless solvates, the diacetone and the etherate. All colourless derivatives receive a lactonoid constitution, whilst the coloured compounds are represented as quinonoid.

Colourless *tetrachlorogallein hydrate*,  $C_{20}H_8O_7Cl_4 \cdot H_2O$ , is obtained by adding water to an acetone solution of the red hydrate, and passing moist carbon dioxide through the solution; after several days the colourless hydrate crystallises in triclinic needles. Chemically its behaviour is almost identical with that of the red hydrate. It loses  $H_2O$  at  $157^\circ$ , and forms tetrachlorogallein. Both hydrates react with dry ammonia to form the same bluish-black *tetra-ammonium* salt as does tetrachlorogallein itself, but whilst the red hydrate absorbs hydrogen chloride to form a red *hydrochloride*,  $C_{20}H_8O_7Cl_4 \cdot HCl \cdot H_2O$ , without loss of water, the colourless hydrate slowly absorbs hydrogen chloride and also loses 1 mol.  $H_2O$ , yielding the red hydrochloride,  $C_{20}H_8O_7Cl_4 \cdot HCl$ , identical with that produced from tetrachlorogallein (*loc. cit.*). This difference in behaviour strikingly confirms the constitutions ascribed to the two hydrates:



Colourless hydrate.



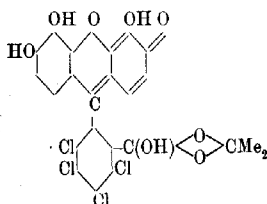
Coloured hydrate.

*Tetrachlorogallein diacetone*,  $C_{20}H_8O_7Cl_4 \cdot 2C_3H_6O$ , separates in almost colourless crystals from a solution of tetrachlorogallein in dry acetone. It loses acetone in a vacuum over phosphoric oxide,

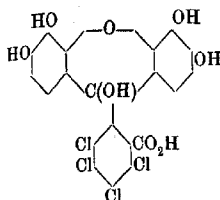
gradually becoming intensely red, and finally, after being heated at  $157^\circ$  in carbon dioxide, colourless again, yielding tetrachlorogallein; the colour is most intense when the composition of the decomposing diacetone, corresponds with the formula  $C_{20}H_8O_7Cl_4 \cdot C_3H_6O$ . In the air the diacetone loses its

acetone and takes up rather more than one molecule of water to form a mixture of red tetrachlorogallein hydrate with a little of the carbinolcarboxylic acid (see below). The behaviour of the diacetone accords with the annexed constitution.

*Tetrachlorogalleincarbinolcarboxylic acid*,  $C_{20}H_{10}O_8Cl_4 \cdot H_2O$ , is obtained as a white precipitate by adding a cold acetone solution of the preceding diacetone (or of either of the hydrates or of anhydrous



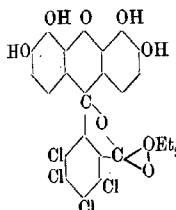
tetrachlorogallein itself) to a large excess of cold acidified water. The substance loses  $\text{H}_2\text{O}$  at  $157^\circ$ , yielding the colourless, anhydrous *carbinolcarboxylic acid* (annexed constitution), which differs from



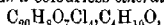
the isomeric red hydrate in that it does not lose more water even at  $203^\circ$ . However, it combines very easily with hydrogen chloride in the cold, forming a red *hydrochloride* (probably the hydrochloride obtained from the red tetrachlorogallein hydrate, since it loses water and hydrogen chloride at  $157^\circ$ , yielding tetrachlorogallein), and with dry ammonia, forming by loss of water the bluish-black tetra-ammonium salt

described above. This confirms Baeyer's statements that all carbinols are colourless, and that colour only appears in consequence of loss of water.

Attempts to crystallise tetrachlorogalleincarbinolcarboxylic acid give a mixture of the colourless and the coloured tetrachlorogallein hydrates; also the action of acetic anhydride produces the colourless tetrachlorogallein tetra-acetate, thus showing that the elimination of water from the carbinol acid does not necessarily give a coloured compound.



When tetrachlorogallein diacetate is shaken with dry ether and filtered, the filtrate yields a colourless *etherate*,



which loses ether extremely easily, and at  $157^\circ$  in carbon dioxide yields a mixture of equal parts of tetrachlorogallein and its carbinolcarboxylic acid. The etherate becomes pink in air, owing to its conversion, by absorption of water and loss of ether, into colourless tetrachlorogallein hydrate, the carbinolcarboxylic acid, and a little of the coloured hydrate. The etherate is given the annexed constitution. C. S.

**New Synthesis of Trihydroxythioxanthones.** FRITZ ULLMANN and MASUO SONE (*Ber.*, 1911, 44, 2146—2148).—When warmed gently with concentrated sulphuric acid, aromatic mercaptans and gallic acid readily condense to form trihydroxythioxanthones. Gallic acid and phenyl mercaptan yield Davis and Smiles' 2 : 3 : 4-trihydroxythioxanthone (*Trans.*, 1910, 97, 1290), the *trimethyl ether* of which has m. p.  $153$ — $154^\circ$ . Gallic acid and *p*-tolyl mercaptan yield 2 : 3 : 4-

*trihydroxy-7-methylthioxanthone*,  $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{CO} \\ \text{S} \end{smallmatrix} \text{C}_6\text{H}(\text{OH})_3$ , yellow needles, darkening above  $240^\circ$ . It forms a reddish-brown solution in dilute alkalis, an orange solution with a faint green fluorescence in concentrated sulphuric acid, and yields with methyl sulphate and potassium hydroxide a *trimethyl ether*, yellow needles, m. p.  $135^\circ$ .

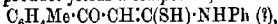
C. S.

**Oxythiophens.** MAURICE LANFRET (*Compt. rend.*, 1911, 153, 73—76).—When thiophen is boiled with hydrogen peroxide (6—13 vols.) two substances are obtained, and may be separated by fractionation. *Dioxythiophen*,  $C_4H_2O_2S$ , has b. p. about  $130^\circ$ ;  $D_{20}^{20}$  1.26; *tetraoxythiophen*,  $C_4H_2O_4S$ , has b. p.  $158$ — $160^\circ$ ,  $D_{20}^{20}$  1.43. The compounds closely resemble one another, and show no phenolic properties; they are colourless liquids with an agreeable odour, unaltered by treatment with sodium, alkali hydroxide, or phenylhydrazine. Nitric or sulphuric acid brings about profound decomposition on boiling. With concentrated sulphuric acid and isatin, they develop a green coloration, destroyed by excess of water. Tetraoxythiophen forms an octabromide,  $C_4O_4SBr_8$ , m. p.  $65$ — $66^\circ$ , by addition and substitution; the existence of this compound indicates that the oxygen in the original substance is united to sulphur.

When the amount of active oxygen in the hydrogen peroxide corresponds with less than 1.5 grams per gram of thiophen, a brown substance is formed, soluble in alkalis. It appears to be a mixture, and under some conditions approximates in composition to the formula  $(C_4H_2OS)_n$ . W. O. W.

**Action of Carbon Disulphide and Potassium Hydroxide on *p*-Tolyl Methyl Ketone and  $\alpha$ -Thienyl Methyl Ketone.** C. KELLER and A. SCHWARZ (*Ber.*, 1911, 44, 1693—1700. Compare Abstr., 1892, 340, 1127; 1904, i, 510; 1905, i, 810; 1909, i, 46, 47).—*p*-Tolyl methyl ketone and  $\alpha$ -thienyl methyl ketone react with carbon disulphide and alkali in much the same manner as acetophenone (Abstr., 1910, i, 390), the products having the characteristics of thiols.

The compound,  $C_{10}H_{10}OS_2 = C_6H_4Me \cdot CO \cdot CH : C(SH)_2$ , obtained from *p*-tolyl methyl ketone, carbon disulphide, finely-powdered potassium hydroxide, and two drops of water by heating on the water-bath and then cooling rapidly, crystallises from light petroleum in glistening, yellow plates, m. p.  $84$ — $85^\circ$ . Carbon dioxide precipitates it from solutions of its alkali salts. The *dimethyl ether*,  $C_{12}H_{14}OS_2$ , forms pale yellow, glistening needles, m. p.  $104$ — $105^\circ$ ; the *dibenzyl ether*,  $C_{24}H_{26}OS_2$ , broad, yellow needles, m. p.  $111.5$ — $112.5^\circ$ , and the *dibenzoyl* derivative,  $C_{24}H_{18}O_2S_2$ , pale yellow crystals, m. p.  $125^\circ$ . When heated for four hours at  $125^\circ$  with 0.5*N* alcoholic potassium hydroxide, the product yields hydrogen sulphide and *p*-toluic acid. Alcoholic ammonia at  $140^\circ$  yields ammonium thiocyanate and *p*-tolyl methyl ketone, and alcoholic hydrochloric acid at  $125^\circ$  yields ethyl mercaptan and *p*-tolyl methyl ketone. When heated on the water-bath with aniline, the product yields a compound,



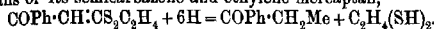
which crystallises from light petroleum in needles, m. p.  $80.5$ — $81.5^\circ$ , and is readily soluble in alkalis. After prolonged heating with aniline, a compound, crystallising in red needles, m. p.  $192.5$ — $193^\circ$ , is formed ( $N = 8.28\%$ ).

The product,  $C_7H_8OS_2$ , obtained from  $\alpha$ -thienyl methyl ketone, crystallises from light petroleum in yellow plates, m. p.  $90$ — $91^\circ$ . The *dimethyl ether*,  $C_9H_{10}OS_2$ , forms compact, yellow needles, m. p.  $96.5^\circ$ , and the *dibenzoyl* derivative,  $C_{21}H_{14}O_2S_2$ , slender, felted, yellow needles, m. p.  $118.5^\circ$ . Its behaviour towards alcoholic solutions of potassium

hydroxide, ammonia, and hydrochloric acid is exactly analogous to the behaviour of the product from *p*-tolyl methyl ketone with these reagents.

The *ethylene ether* of the product previously described (Abstr., 1910, i, 391),  $\text{COPh}\cdot\text{CH}\cdot\text{C} \begin{smallmatrix} \text{S}\cdot\text{CH}_2 \\ \text{S}\cdot\text{CH}_2 \end{smallmatrix}$ , crystallises from light petroleum in

long, pale yellow needles, m. p.  $80^\circ$ . Its solution in concentrated nitric acid has a blue to cherry-red colour, and that in concentrated sulphuric acid a deep yellow colour. When reduced with zinc dust and sodium hydroxide solution, the ether yields propiophenone, detected by means of its semicarbazone and ethylene mercaptan,



The *propylene ether*,  $\text{COPh}\cdot\text{CH}\cdot\text{CS}_2\text{C}_3\text{H}_7$ , m. p.  $52-53^\circ$ , is reduced in an exactly similar manner, and these reactions are used as an argument in favour of the unsaturated dithiol structure previously given to the condensation product from acetophenone. J. J. S.

**Cinchona Alkaloids. XIII. Fluorescence Phenomena with Cinchona Alkaloids.** PAUL RABE and OSWALD MARSCHALL (*Annalen*, 1911, 382, 360-364. Compare Stokes, *Jahresber.*, 1864, 100).—The phenomena of fluorescence of cinchona alkaloids have been examined qualitatively in order to establish relationships between constitution and fluorescence. The experiments were made with sunlight, light from a uviolet lamp, and the ultra-violet rays from an arc lamp. The general method adopted was similar to that used by Tswett (Abstr., 1901, ii, 298; compare also Stobbe, *ibid.*, 1909, ii, 282).

The results show that slight differences in arrangement of the atoms within the molecule, as exemplified by cases of stereoisomerism, produce an appreciable effect on the fluorescence; the examples quoted are the following pairs of substances, which were examined in the solid form by filtered ultra-violet light: cinchonine, blue; cinchonidine, pale blue; quinine, intense blue; quinidine, light blue; quinine hydrochloride, intense blue; quinidine hydrochloride, yellowish-red; deoxyquinine, reddish-blue; deoxyquinidine, sky-blue.

In all cases the fluorescence is more pronounced when working with ultra-violet light than with sunlight; the quality and intensity of the fluorescence varies with the solvent, but no generalisations can be drawn between the two. When water is added gradually to an alcoholic solution, it frequently first produces an increase and ultimately a diminution of the fluorescence.

With quinine salts an important factor is the acid with which the base is combined; thus, when 0.1 gram of the base is dissolved in 20 c.c. of 0.1*N*-acid, the following results are obtained: sulphuric, nitric, phosphoric, hydrofluoric, and trichloroacetic give strongly fluorescent solutions, tartaric and acetic moderately strongly fluorescent, and the halogen hydric acids very feebly fluorescent solutions. J. J. S.

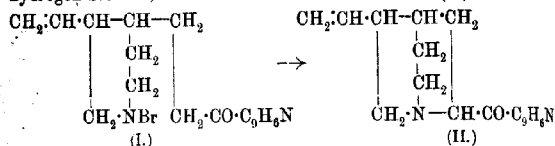
**Cinchona Alkaloids. XIV. Decomposition of Oximinocinquinotoxine.** PAUL RABE and ERNST MILARCH (*Annalen*, 1911, 382, 365-368. Compare Rabe and Ackermann, Abstr., 1907, 4, 546).—The products obtained by shaking phosphorus pentachloride with an

ice-cold chloroform solution of oximinoquinotoxine (Rohde and Schwab, Abstr., 1905, i, 228) and then pouring on to ice and water are quinic acid and the nitrile of meroquinine. The oximino-derivative of the tertiary methylquinotoxine behaves in a similar manner, yielding quinic acid and the nitrile of *N*-methylmeroquinine (Rabe and Ritter, Abstr., 1905, i, 811).

J. J. S.

**Cinchona Alkaloids. XV. Partial Synthesis of Cinchonine.** PAUL RABE (*Ber.*, 1911, 44, 2088—2091).—An account of the transformation of cinchotoxine into cinchonine.

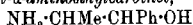
*N*-Bromocinchotoxine (I), obtained by the action of aqueous sodium hypobromite on cinchotoxine in dilute hydrochloric acid solution at the ordinary temperature, crystallises from alcohol or ether in colourless, elongated prisms, m. p. 153°. It differs from cinchotoxine in being without action towards litmus and methyl iodide. When treated in hot alcoholic solution with sodium ethoxide, it loses hydrogen bromide, and is converted into cinchoninone (II):



\* The reduction of cinchoninone to cinchonine has been described previously (Rabe and Buchholz, Abstr., 1908, i, 100).

F. B.

**Ephedrine and  $\psi$ -Ephedrine.** ERNST SCHMIDT [with W. CALLIES] (*Apoth. Zeit.*, 1911, No. 37; Reprint 3 pp.).—A preliminary note necessitated by work published by Emde, Fourneau, and Rabe and Hallensleben (compare this vol., i, 396). The synthesis of a base isomeric with ephedrine or  $\psi$ -ephedrine starts from phenyl  $\alpha$ -bromoethyl ketone. This is converted into *phenyl- $\alpha$ -aminoethyl ketone*,  $\text{NH}_2\cdot\text{CHMe}\cdot\text{COPh}$  (*hydrochloride*, m. p. 179°; *nitrate*, m. p. 139—140°; *picrate*, m. p. 160°; *platinichloride*, m. p. 200°; *aurichloride*, m. p. 151°; *mercurichloride*, m. p. 126° or 165°; *stannichloride*, m. p. 219—220°), which is reduced by sodium amalgam in faintly acid solution at 0° to *phenyl- $\alpha$ -aminosthylcarbinol*,

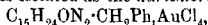


(*hydrochloride*, m. p. 165°; *aurichloride*, m. p. 130°; *platinichloride*, m. p. 187—188°). This carbinol forms by direct methylation a quaternary base, an aqueous solution of which, by distillation, yields trimethylamine and an oily substance free from nitrogen. The substance  $\text{NHMe}\cdot\text{CHMe}\cdot\text{CHPh}\cdot\text{OH}$  is obtained by treating phenyl  $\alpha$ -bromoethyl ketone with methylamine and reducing the product with sodium amalgam in faintly acid solution.

$\omega$ -Aminobenzyl methyl ketone yields by reduction the *carbinol*,  $\text{NH}_2\cdot\text{CHPh}\cdot\text{CHMe}\cdot\text{OH}$  (*hydrochloride*, m. p. 165—167°), which reacts with  $\alpha$ -ethyl iodide in methyl alcohol to form, ultimately, a quaternary base, the distillation of which yields trimethylamine and an oil, as yet unexamined.  $\omega$ -Bromobenzyl methyl ketone and

methylamine yield a base,  $\text{NHMe}\cdot\text{CHPh}\cdot\text{COMe}$  (hydrochloride, m. p. above  $300^\circ$ ), which is converted by reduction into *o*-methylaminobenzyl-methylcarbinol,  $\text{NHMe}\cdot\text{CHPh}\cdot\text{CHMe}\cdot\text{OH}$ , an oil the hydrochloride of which has m. p.  $190^\circ$ . C. S.

*d*-Lupanine. AUGUST BECKEL (*Arch. Pharm.*, 1911, 249, 329—353).—A chemical relationship between lupanine,  $\text{C}_{15}\text{H}_{24}\text{ON}_2$ , and sparteine,  $\text{C}_{15}\text{H}_{28}\text{N}_2$ , has often been assumed in consequence of the similarity in composition and the occurrence of both alkaloids in the seeds of lupines. The two nitrogen atoms in sparteine are tertiary, and the alkaloid behaves as a diacidic base and forms two isomeric methiodides. The author has examined very thoroughly the behaviour of *d*-lupanine (isolated as the hydrochloride from the seeds of *Lupinus angustifolius*) with methyl iodide, with and without a solvent, at the ordinary temperature, at  $100^\circ$ , and even at  $190^\circ$ , but in no circumstances has a methiodide been isolated other than that described in the literature (m. p.  $240^\circ$ , decomp.); their interaction at  $150^\circ$  results in a partial, at  $190^\circ$  in a complete, conversion of the methiodide into lupanine hydriodide. Lupanine methiodide does not form an additive compound with hydriodic acid. Lupanine an ethyl iodide, alone or in boiling alcohol, yield lupanine hydriodide. Benzyl bromide, but not benzyl chloride, forms an additive compound with lupanine, which is isolated as the aurichloride,



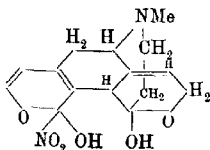
m. p.  $186\text{--}187^\circ$  (decomp.) (platinichloride, m. p.  $203\text{--}204^\circ$ , decomp.). Lupanine methiodide does not react with ethyl iodide or benzyl bromide at the ordinary temperature or at  $100^\circ$ .

*d*-Lupanine does not decolorise acidified potassium permanganate, and can be titrated as a mono-acidic base. C. S.

Morphine. I. HEINRICH WIELAND and PAUL KAPPELMEIER (*Annalen*, 1911, 382, 306—339).—Knorr's formula for morphine is discussed. Most of the methods used in connexion with the elucidation of the constitution of morphine have been based on Hofmann's degradation process involving a rupture of the nitrogen ring. The author has attempted to use the process of oxidation, but it has not been found possible to obtain definite homogeneous products by direct oxidation. Attempts to obtain acids from 2-nitrosomorphine by hydrolysing to the 2:3-quinone and subsequent oxidation also proved unsuccessful. The oxidation of 2-amino- and 2-hydroxy-morphine also gave negative results.

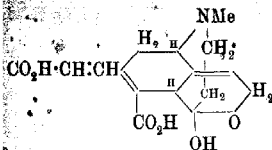
It has been found possible to rupture the morphine ring by means of nitrous gases. When these gases are passed into an aqueous solution of a morphine salt, 2-nitrosomorphine is formed together with the unstable nitrate of a base,  $\text{C}_{17}\text{H}_{19}\text{O}_6\text{N}_2$ .

The annexed structural formula suggested for the base is that of a quin-nitrole (Zincke, *Abstr.*, 1905, i, 881). The reaction consists in the addition of nitric acid to one ring, of the hydro-

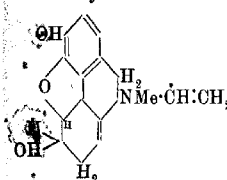


lytic rupture of the oxygen bridge and the oxidation of the secondary alcoholic group to a ketonic group.

When an aqueous solution of the unstable nitrate is warmed, a 30% yield of the colourless nitrate of the base  $C_{17}H_{18}O_4N$  is obtained. This compound has acidic properties, is termed morphinic acid, and is regarded as formed by the oxidation of the o-quinone, from which the quinnitrole is derived, and is therefore represented by the annexed formula.



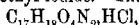
The adjacent structural



formula for morphine is suggested. According to this the nitrogen atom is attached to carbon atom 9 of the phenanthrene nucleus, but contains a free vinyl group. The actual ring formation occurs with the aid of this vinyl group in the conversion of morphine into methylmorphimethine, apomorphine, thebaine, etc. This formula accounts for the readiness with which many

morphine derivatives combine with water, and also for the readiness with which the  $-N \cdot C \cdot C-$  group is eliminated from morphine.

The compound described by Mayer (*Ber.*, 1871, 4, 121) as nitroso-morphine is probably morphine nitrite, and differs entirely from 2-nitrosomorphine, which is formed when nitrous fumes are passed into a suspension of morphine hydrochloride in water at  $-2^\circ$  to  $-3^\circ$ ; the salt dissolves gradually, the liquid turns orange-red, and the nitroso-compound can be isolated as its sodium derivative,  $C_{17}H_{17}O_4N_2Na \cdot H_2O$ , by the addition of cold 20% sodium hydroxide solution. This derivative crystallises from 90% alcohol in brilliant, dark red needles, and turns black when heated, but has no definite m. p. The silver derivative forms an insoluble, almost black precipitate, m. p.  $181-182^\circ$  (decomp.), but does not react with methyl iodide. The hydrochloride,



forms lemon-yellow needles, m. p.  $248^\circ$  (decomp.). 2-Nitrosomorphine,  $C_{17}H_{18}O_4N_2 \cdot H_2O$ , obtained by the action of acetic acid on the sodium derivative or of ammonia on the hydrochloride, crystallises from boiling alcohol in polymorphous forms; the more stable form consists of slender, dark orange-red needles, m. p.  $225^\circ$  (decomp.). It reduces neither Fehling's solution nor ammoniacal silver nitrate, is not appreciably decomposed by acids or alkalis, and its alkali salts give a dark green coloration with ferric chloride. The minutest traces of morphine react with a drop of sodium nitrite solution, yielding a yellow coloration which turns to orange on the addition of alkali, and the reaction is an extremely delicate one for detecting morphine. When reduced with tin and hydrochloric acid, the nitroso-compound yields 2-aminomorphine,  $C_{17}H_{20}O_4N_2 \cdot H_2O$ , which forms colourless, glistening crystals or quadratic plates, m. p.  $258^\circ$ . The hydrochloride,

$C_{17}H_{20}O_3N_2 \cdot 2HCl$ , is readily soluble in water; and has  $[\alpha]_D - 90^\circ$ ; the *picrate* forms yellow needles, decomposing at  $172^\circ$ .

The amino-compound is readily diazotised, yielding an *o*-diazomorphine anhydride; the *hydrochloride*,  $C_{17}H_{17}O_3N_3 \cdot HCl$ , is formed when the amino-compound is suspended in alcohol, treated with alcoholic hydrogen chloride and ethyl nitrite, and precipitated by the addition of ether. The dry salt decomposes at  $98^\circ$ . When warmed with alcohol, the diazo-compound regenerates morphine, but it has not been found possible to obtain pure 2-hydroxymorphine.

Morphine as a phenol couples with diazonium salts, yielding azo-dyes. *Benzeneazomorphine*,  $C_{23}H_{23}O_3N_3$ , crystallises from alcohol in slender, orange-yellow needles, m. p.  $175^\circ$  (decomp.). Its solutions in acids are orange-brown, and in alkali, blood-red. When reduced with stannous chloride and hydrochloric acid, it yields aniline and aminomorphine.

2-Aminocodeine,  $C_{18}H_{20}O_3N_2$ , obtained by reducing the corresponding nitro-derivative, crystallises from absolute alcohol, has m. p.  $226^\circ$ , and does not possess reducing properties. Its *hydrochloride* is amorphous, and is readily diazotised to a diazonium salt, which couples with an alkaline solution of  $\beta$ -naphthol, yielding a brilliant red dye. When a solution of the diazonium salt is heated, small amounts of 2-hydroxycodeine,  $C_{18}H_{21}O_3N$ , are obtained in colourless needles, m. p.  $176^\circ$ .

2-Nitroso- and 2-amino-morphine are readily transformed into the corresponding apomorphine compounds by the loss of water, for example, when heated with 30% hydrochloric acid at  $145^\circ$  and  $130^\circ$  respectively. 2-Nitrosoapomorphine *hydrochloride*,  $C_{17}H_{16}O_3N_2 \cdot HCl$ , crystallises from hot water in felted, yellowish-green needles, changes colour at  $200^\circ$ , but has no definite melting point, and reduces ammoniacal silver nitrate, but not Fehling's solution. The free base,  $C_{17}H_{16}O_3N_2 \cdot H_2O$ , crystallises from absolute alcohol in red needles, which are not molten at  $300^\circ$ . 2-Aminoapomorphine *hydrochloride*,  $C_{17}H_{15}O_3N_2 \cdot 2HCl$ , crystallises from dilute hydrochloric acid in colourless, felted needles, m. p.  $260-265^\circ$ . It reduces hot Fehling's solution, and with ferric chloride gives a deep violet coloration, which is rapidly transformed to an olive-green. The base is more sensitive to oxidation than apomorphine itself; it has been obtained as a colourless, amorphous mass, which turns violet-coloured on exposure to the air.

*Morphineguinnitrate*,  $C_{17}H_{18}O_6N_2 \cdot HNO_3 \cdot H_2O$ , crystallises in brilliant, glistening, orange-yellow prisms when an excess of nitrous fumes is passed into an aqueous suspension of morphine. It cannot be recrystallised, and when its concentrated aqueous solution is warmed, morphinic acid (33%) is obtained, together with dark red, amorphous, by-products. *Morphinic acid nitrate*,  $C_{17}H_{19}O_6N_2 \cdot HNO_3 \cdot H_2O$ , crystallises from hot water in colourless prisms, which turn brown on exposure to light. It has no definite melting point, does not give a coloration with ferric chloride, but reduces hot Fehling's solution. *Morphinic acid*, obtained by decomposing the nitrate with concentrated sodium acetate solution, is characterised by the deep green colour which it gives when warmed with water, and this, with a few drops of hydrochloric acid, changes to a cherry-red.



The *hydrochloride*,  $C_{17}H_{19}O_6N.HCl.2H_2O$ , crystallises in colourless needles.

Chloromorphine, prepared by the action of thionyl chloride on morphine, reacts with diethylamine at  $100^\circ$ , yielding *diethylaminomorphine*,  $C_{21}H_{28}O_2N_2$ , which crystallises from absolute alcohol in colourless prisms, m. p.  $203^\circ$ . The base is soluble in strong alkalis, but not in ammonia solution. The *hydrochloride* has m. p.  $268^\circ$  (decomp.), and gives a blue coloration with ferric chloride. The *methiodide*,  $C_{22}H_{31}O_2N_2I$ , has m. p.  $268^\circ$  (decomp.).

*Dichlorodiacetylmorphine*,  $C_{21}H_{21}O_6NCl_2$ , obtained by the action of chloroacetyl chloride on anhydrous morphine, crystallises from ether, has m. p.  $135^\circ$ , and readily loses one chloroacetyl group, yielding *chloroacetylmorphine*,  $C_{19}H_{20}O_4NCl$ , which crystallises from alcohol in colourless needles, m. p.  $234^\circ$  (decomp.).

*Benzenesulphonylmorphine benzenesulphonate*,  
 $C_{23}H_{23}O_5NS.C_6H_5.SO_3H$ ,  
 crystallises from hot water in slender needles, m. p.  $140^\circ$ . The base has m. p.  $165^\circ$ . J. J. S.

**Strychnine Alkaloids. XI. The Brucine-Nitric Acid Reaction.** Preparation of a New Alkaloid, *Bisapomethylbrucine*. HERMANN LEUCHS and RUDOLPH ANDERSON (*Ber.*, 1911, 44, 2136—2145).—The colour reaction with nitric acid is shown, not only by brucine itself, but also by almost all its known derivatives and degradation products; in two instances, *brucinesulphonic acid* and *brucinolone*, substances have been isolated which behave like quinones, in that they can be reduced to the corresponding quinols. The present paper deals with the quinone and quinol corresponding with brucine itself.

Brucine is digested at  $0^\circ$  with 5*N*-nitric acid for half an hour, the red solution is reduced by sulphurous acid at  $0^\circ$ , and the quinol, *bisapomethylbrucine*,  $C_{21}H_{22}O_4N_2$ , prisms darkening at  $260^\circ$  and decomp.  $285^\circ$ , is purified by means of the *hydrochloride*,  $C_{21}H_{23}O_4N_2.HCl$ . The base develops an indigo-blue coloration with ferric chloride, reduces silver nitrate, and is readily soluble in alkalis.

By treating the red solution of brucine in nitric acid with an excess of cold saturated potassium hydrogen carbonate, a red substance,  $C_{21}H_{21}O_6N_3$ , is obtained, which is converted by chloroform and petroleum into the hydrated *quinone*,  $C_{21}H_{20}O_4N_2.H_2O$ , dark red needles, from which only one-half of the water can be expelled by intense drying. The anhydrous *quinone*,  $C_{21}H_{20}O_4N_2$ , red needles, is obtained by oxidising *bisapomethylbrucine* with chromic and sulphuric acids, whereby a red, crystalline substance,  $C_{21}H_{20}O_4N_2.H_2CrO_4.HCl$ , isolated by means of 5*N*-hydrochloric acid, is first obtained, which is converted into the anhydrous quinone by aqueous sodium hydrogen carbonate. After having once been isolated, the quinone and also its hydrate are not readily reduced to *bisapomethylbrucine*. C. S.

**The Pyridine Compounds of the Tin Halides.** PAUL PFEIFFER [with B. FRIEDMANN, R. LEHNARDT, H. LUFTESTEINER, RUDOLF PRADE, and K. SCHNURMANN] (*Zeitsch. anorg. Chem.*, 1911, 71, 97—120. Compare *Abstr.*, 1910, i, 852).—Tin forms four series of pyridine

compounds:  $\text{SnX}_4\text{Py}_2$ ,  $\text{SnRX}_3\text{Py}_2$ ,  $\text{SnR}_2\text{X}_2\text{Py}_2$ , and  $\text{SnR}_2\text{XPy}_2$ , giving, as before, the co-ordination number six, and confirming the constitutional formulae previously given for the alkylated and phenylated compounds. Only the diphenylated stannic halides yield in addition additive compounds containing more than 2 mols. of pyridine. The iodides are also exceptional, the quantity of pyridine added depending on the number of iodine atoms. The difference is due to the additive power of the iodine atom.

*Dipyridine tin tetrabromide*,  $\text{SnBr}_4\text{Py}_2$ , prepared by adding dry pyridine to well cooled tin tetrabromide, is a white powder. Tin tetraiodide yields an unstable compound,  $\text{SnI}_4\text{Py}_2\cdot 3\text{Py}$ . *Dipyridine tin methyl trichloride*,  $\text{SnMeCl}_3\text{Py}_2$ , prepared from an ethereal solution of tin methyl chloride, and the *tribromide*,  $\text{SnMeBr}_3\text{Py}_2$ , are also amorphous. The tri-iodide yields a yellow additive compound,  $\text{SnMeI}_3\text{Py}_2\cdot 2\text{Py}$ . The following compounds have also been prepared: *dipyridine tin dimethyl dichloride*,  $\text{SnMe}_2\text{Cl}_2\text{Py}_2$ , colourless crystals, m. p.  $163^\circ$  (decomp.); the *dibromide*,  $\text{SnMe}_2\text{Br}_2\text{Py}_2$ , m. p.  $172^\circ$  (decomp.), and the *di-iodide*,  $\text{SnMe}_2\text{I}_2\text{Py}_2$ , m. p.  $147^\circ$  (decomp.).

*Dipyridine tin dipropyl dichloride*,  $\text{SnPr}_2\text{Cl}_2\text{Py}_2$ , forms colourless, glistening needles, m. p.  $114^\circ$ ; the *dibromide* has m. p.  $128^\circ$ . *Dipyridine tin dibutyl dichloride*,  $\text{Sn}(\text{C}_4\text{H}_9)_2\text{Cl}_2\text{Py}_2$ , has m. p.  $65-66^\circ$ , and the *dibromide*, m. p.  $77-78^\circ$ .

*Dipyridine tin diphenyl dichloride*,  $\text{SnPh}_2\text{Cl}_2\text{Py}_2$ , is stable in air and has m. p.  $151^\circ$ . It also forms an additive compound with 2 mols. of pyridine, m. p.  $155-156^\circ$  (decomp.). The *dibromide*,  $\text{SnPh}_2\text{Br}_2\text{Py}_2$ , forms large crystals, m. p.  $155^\circ$  (decomp.), and also yields an additive compound, m. p.  $160^\circ$  (decomp.), with 2 mols. of pyridine. *Dipyridine tin ditolyl dibromide*,  $\text{Sn}(\text{C}_6\text{H}_4\text{Me})_2\text{Br}_2\text{Py}_2$ , has m. p.  $172-176^\circ$ ; *dipyridine tin triphenyl chloride*,  $\text{SnPh}_3\text{ClPy}_2$ , has m. p.  $81-84^\circ$ , and the *bromide*, m. p.  $78-84^\circ$ . C. H. D.

**Preparation and Fission of Dihydroindole.** JULIUS VON BRAUN and WLADISLAUS SOBECKI (*Ber.*, 1911, 44, 2158-2161).—Dihydroindole, obtained from indole by Carrasco's electrolytic method, forms a *benzenesulphonyl* derivative, fine needles, m. p.  $133^\circ$ , and a *benzoyl* derivative, m. p.  $118^\circ$ . The latter is converted by phosphorus pentachloride in the usual manner into *o*- $\beta$ -chloroethylbenzanilide,  $\text{CH}_3\text{Cl}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHBz}$ , m. p.  $120^\circ$ , in 30% yield. C. S.

**Preparation of  $\beta$ -Iodoindole.** ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1911, 73, 128-130. Compare Abstr., 1909, i, 512).—2-Iodoindole can be prepared by the action of a solution of iodine in potassium iodide on a solution of indole and potassium hydroxide in water, and just sufficient alcohol to keep the compound in solution. It forms snow-white crystals, m. p.  $72^\circ$ , and turns black on exposure to the air. Scatole (2-methylindole) and tryptophan cannot be converted into iodo-derivatives by either method. J. J. S.

**Dihydroquinaldine Bases.** GUSTAV HELLER [with SIEGMUND SCHMEJLA] (*Ber.*, 1911, 44, 2106-2115).—It has been shown previously (Heller and Sourlis, Abstr., 1908, i, 914) that 2-methyl-

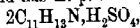
quinoline, when heated with zinc dust and hydrochloric acid, yields 2-methyldihydroquinoline. This method of reduction has now been applied to the preparation of the dihydro-derivatives of several isomeric methylquinolines and dimethylquinolines. These dihydro-bases are all bimolecular, and cannot be further reduced to the corresponding tetrahydro-compounds. From their indifference towards methyl iodide, and the fact that they yield neither nitrosoamines nor acetyl derivatives, the authors draw the conclusion that the nitrogen atom in these compounds is no longer tervalent. When heated with mercuric oxide in cumene solution or with chromium trioxide in glacial acetic acid solution, the dihydro-bases are oxidised to the corresponding quinolines.

2-Methyldihydroquinoline hydrochloride,  $C_{10}H_{11}N \cdot HCl$ , crystallises in lustrous needles, which become brown at  $210^\circ$ , and have m. p.  $250^\circ$ ; the sulphate,  $2C_{10}H_{11}N \cdot H_2SO_4$ , crystallising in lustrous leaflets, becomes brown at  $210^\circ$ , and decomposes at  $240^\circ$ .

2-Methyldihydroquinoline condenses with chloral hydrate, formaldehyde, and phthalic anhydride, but the products thus formed could not be obtained crystalline. When treated with bromine in chloroform solution, it yields dibromo-2-methyldihydroquinoline,  $C_{10}H_9NBr_2$ . This crystallises in lustrous, colourless needles, m. p.  $242^\circ$  (decomp.), and is not oxidised by mercuric oxide. Its stability towards alcoholic potassium hydroxide and reducing agents indicates that the bromine atoms have probably entered the benzene nucleus. Unsuccessful attempts have been made to synthesise this dihydro-compound from *o*-nitrostyryl methyl ketone (Baeyer and Drewsen, Abstr., 1883, 341). The latter compound, when treated with bromine in glacial acetic acid solution, yields the dibromide,  $NO_2 \cdot C_6H_4 \cdot CHBr \cdot CHBr \cdot COMe$ , which crystallises in colourless needles, m. p.  $102^\circ$ , and is reduced by zinc and acetic acid to 2-methylquinoline and 2-methyltetrahydroquinoline.

2:8-Dimethyldihydroquinoline crystallises in colourless needles, m. p.  $216-217^\circ$ , and has no basic properties. When treated with bromine in hot alcoholic or glacial acetic acid solution it yields a tetrabromo-derivative,  $C_{11}H_9NBr_4$  (?), which forms sulphur-yellow crystals, m. p.  $171-172^\circ$ . Bromination in dilute alcoholic solution results in the formation of a tribromo-derivative,  $C_{11}H_{10}NBr_3$ , m. p.  $121-122^\circ$ , whilst in chloroform or benzene solution the action of bromine yields a substance, m. p.  $240-250^\circ$ , containing only two atoms of bromine in the molecule.

2:6-Dimethyldihydroquinoline has m. p.  $143^\circ$ ; the hydrochloride forms white needles, which become brown at  $205^\circ$ , and have no definite m. p.; the hydrobromide, crystallising in lustrous needles, becomes brown at  $215^\circ$ , and has m. p.  $260^\circ$ ; the sulphate,



has m. p.  $220^\circ$  (decomp.), becoming brown at  $206^\circ$ .

The behaviour of 2:6-dimethyldihydroquinoline towards bromine resembles that of the isomeric 2:8-compound; the tetrabromo-derivative,  $C_{11}H_9NBr_4$ , obtained by bromination in hot glacial acetic acid solution, crystallises in pale yellow needles, m. p.  $172^\circ$ .

2:7-Dimethyldihydroquinoline is amorphous, and on account of its feebly basic properties could not be further purified.

The reduction of quinoline by zinc and hydrochloric acid takes place at the ordinary temperature, dihydroquinoline together with a small quantity of tetrahydroquinoline being produced.

8-Methyldihydroquinoline,  $C_{10}H_{11}N$ , has m. p.  $144^{\circ}$ ; the hydrochloride, m. p.  $278^{\circ}$ .

6-Methyldihydroquinoline melts indefinitely at  $60-105^{\circ}$ , forms no salts, and therefore could not be further purified.

By distilling dihydroglauconic acid or by heating 2-methylquinoline hydrochloride with zinc dust, Doebner (Abstr., 1898, i, 384) obtained a substance which he considered to be 2-methyldihydroquinoline. According to the author this consists of 2-methylquinoline, whilst Doebner's dihydro-2:6-dimethylquinoline (Abstr., 1900, i, 313) is identical with 2:6-dimethylquinoline. F. B.

Cyanodihydrocyclic Amines. IV. Synthesis of Cinchonic Acid. ADOLF KAUFMANN and ROBERT WIDMER [with ALBERTO ALBERTINI] (*Ber.*, 1911, 44, 2058—2065).—On oxidation of 4-cyano-

1-methyldihydroquinoline,  $C_6H_4 \begin{smallmatrix} CH(CN):CH \\ | \\ NMe-CH \end{smallmatrix}$ , with alcoholic iodine solution, it is readily converted into the methiodide of 4-cyanoquinoline,  $C_6H_4 \begin{smallmatrix} C(CN):CH \\ | \\ NMeI:CH \end{smallmatrix}$ , which, on hydrolysis, forms the meth-

iodide of cinchonic acid,  $C_6H_4 \begin{smallmatrix} C(CO_2H):CH \\ | \\ NMeI=CH \end{smallmatrix}$ . Both iodides are oxidised by alkaline ferri cyanide solution to known  $\alpha$ -quinolones, and the betaine of 1-methylcinchonic acid is obtained on treating the methiodide with moist silver oxide.

4-Cyanoquinoline is conveniently prepared by heating 4-cyanoquinoline methiodide in a stream of carbon dioxide at  $210-220^{\circ}$ , when methyl iodide is eliminated, and the nitrile sublimes in long, colourless needles, m. p.  $95^{\circ}$ .

In general, cyclaminones when distilled with zinc dust form cyclamine bases; thus, 4-cyano-1-methyl-2-quinolone yields the nitrile of cinchonic acid.

Cyanodihydroacridines are unaffected by alcoholic iodine solution, and the cyano-group cannot be displaced by bromine, which, however, forms a dibromo-derivative, dibromocyanophenylmethyldihydroacridine, crystallising in colourless, cubic crystals, m. p.  $208-209^{\circ}$ . From analogy to the experiments of Dunstan and Oakley (Abstr., 1906, i, 383), the bromine atoms are considered to occupy the 3:6-positions.

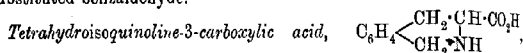
4-Cyanoquinoline methiodide forms red needles, which darken at  $180^{\circ}$ , m. p.  $216^{\circ}$  (decomp.).

On bromination of phenylmethyldihydroacridone, the methobromide of dibromophenylacridine is obtained in orange-yellow needles, m. p.  $274^{\circ}$  (decomp.). Potassium cyanide converts it into the dibromocyanophenylmethyldihydroacridine just described. With alcoholic potassium hydroxide, a reddish-violet coloration is obtained, and yellow needles separate of the ethyl ether of 3:7-dibromo-5-phenyl-10-methyldihydroacridinol; they become violet at  $170^{\circ}$ , m. p.  $192-195^{\circ}$ .

(decomp.). 3:7-Dibromo-5-cyano-5:10-dimethyldihydroacridine forms strongly refractive cubes, which blacken at 220°, m. p. 228°. E. F. A.

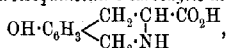
**Formation of isoquinoline Derivatives by the Action of Methylal on Phenylethylamine, Phenylalanine, and Tyrosine.** AMÉ PICTET and THEODOR SPENGLER (*Ber.*, 1911, 44, 2030—2036). — Tetrahydroisoquinoline derivatives are obtained directly on condensing substituted phenylethylamines with aldehydes instead of with acids, as in the Bischler-Napieralski synthesis, which leads to unsaturated isoquinolines. Thus from formaldehyde and  $\beta$ -phenylethylamine, tetrahydroisoquinoline is obtained without difficulty, and the reaction gives still better results with phenylalanine and tyrosine, which yield with formaldehyde, tetrahydro- and hydroxy-tetrahydro-isoquinolinecarboxylic acids.

In view of the fact that all these substances are natural plant products, it is very probable that a similar condensation takes place in the plant, and that the relatively simple tetrahydroisoquinoline compounds formed after loss of the carboxyl group become methylated and undergo further complication until the various isoquinoline alkaloids are obtained. The latter may now be regarded as modified degradation products of vegetable protein. Such alkaloids as laudanosine represent a primary condensation of amino-acid and formaldehyde, and a secondary condensation of this product with a substituted benzaldehyde.



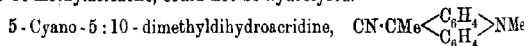
prepared from phenylalanine and methylal, crystallises in large, nacreous, colourless plates, m. p. 311° (decomp.). On heating above the melting point, tetrahydroisoquinoline is formed.

7-Hydroxytetrahydroisoquinoline-3-carboxylic acid,



forms a colourless, microcrystalline precipitate, m. p. 336—338° (decomp.). When heated, a secondary base, probably 7-hydroxytetrahydroisoquinoline is obtained, b. p. 210—220°/18 mm.; the picrate has m. p. 198—201°. The hydrochloride, when distilled with zinc dust gives isoquinoline. E. F. A.

**Cyanodihydrocyclic Amines. III.** ADOLF KAUFMANN and ALBERTO ALBERTINI [with ROBERT WIDMER] (*Ber.*, 1911, 44 2052—2058. Compare Abstr., 1909, i, 606, 958).—5-Cyano-5-phenyl dihydroacridine, probably on account of steric hindrance, could not be converted into the corresponding acid, and, similarly, 5-cyano 10-methyldihydroacridine, on account of the readiness of its oxidation to 10-methylacridone, could not be hydrolysed.



however, yields a carboxylic acid, from which carbon dioxide is eliminated on recrystallisation, and the corresponding dihydroacridine,  $\text{CHMe} \begin{array}{l} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} \text{NMe}$ , obtained.

10-*Methylacridine tartrate* crystallises in green needles of silky lustre, m. p. 153—154° (decomp.). The picrate crystallises with a molecule of alcohol in greenish-yellow needles, m. p. 213—214° (Decker gives 220—221°). The *mercurichloride* forms yellow needles, m. p. 258°; the methiodide golden, glistening platelets, decomp. 200°, m. p. 235—245° (Bernthsen, 185°); the *methochloride* separates in glistening, yellow platelets, m. p. 200°, and gives a yellow crystalline precipitate, m. p. 252—255°, with platinum chloride and brown needles, m. p. 193—194° (explosively), with picric acid.

5-Cyano-5:10-dimethyldihydroacridine, formed by the interaction of methylacridine methochloride and potassium cyanide, separates in colourless crystals, m. p. 123°. The *picrate* crystallises in dark brown plates, m. p. 138—139°.

5-Cyano-10-methyl-5-benzoyldihydroacridine crystallises in colourless needles, m. p. 125°.

5:10-Dimethyldihydroacridine-5-carboxylic acid, prepared by hydrolysis of the cyano-compound with alcoholic potassium hydroxide, crystallises in colourless, glistening plates, which blacken at 130°, m. p. 160° (decomp.). Carbon dioxide is readily eliminated, and 5:10-dimethyldihydroacridine obtained in lanceolate, yellow crystals, m. p. 137° (compare Freund and Bode, Abstr., 1909, i, 514).

E. F. A.

Action of Hydrazine on Carbonyl Compounds. HERMANN STAUDINGER and OTTO KUPFER (*Ber.*, 1911, 44, 2197—2212).—Curtius and his co-workers found that the products obtained from hydrazine and ordinary aldehydes or ketones differed greatly in behaviour from those produced by the interaction of hydrazine and benzil or  $\alpha$ -ketonic esters; the former class, therefore, were regarded as hydrazones,  $>C:N:NH_2$ , and the latter as derivatives of hydrazimethylene,

$>C \begin{smallmatrix} NH \\ \diagup \\ NH \end{smallmatrix}$ . The authors now show that the members of both classes all behave alike under suitable conditions, and are therefore constituted alike, although they are unable to state whether the substances are hydrazones or hydrazimethylenes. One of the chief criteria of members of the second class is their oxidation to azomethylenes,

$>C \begin{smallmatrix} N \\ \diagup \\ N \end{smallmatrix}$ , by mercuric oxide. However, the hydrazones of fluorenone,

dimethoxybenzophenone (*dimethoxybenzophenonehydrazone* has m. p. 84—86°), benzophenone, and acetophenone also yield azomethylene derivatives, which decompose in various ways according to their varying stability; these decompositions are initially the formation of nitrogen and the group  $RR'C<$ , which, by intramolecular change, polymerisation, or interaction with undecomposed azomethylene, may yield non-nitrogenous or nitrogenous compounds. The action of iodine on these azomethylene derivatives also starts with the formation of nitrogen and the group  $RR'C<$ , which then undergoes change as above or unites with iodine to form substituted methylene iodides.

*Diphenyleneazomethylene*,  $\begin{smallmatrix} C_6H_4 \\ \diagup \\ C_6H_4 \end{smallmatrix} >C \begin{smallmatrix} N \\ \diagup \\ N \end{smallmatrix}$ , m. p. 94—95°, dark red

needles, is unimolecular (so also are all other azomethylene derivatives); it yields bisdiphenylene-ethylene when decomposed by heat at 130–140° (in the presence of a little benzene or ether), by iodine in boiling alcohol, or by hydrogen bromide in boiling xylene, and is reduced to fluorene by zinc and alcoholic sodium hydroxide.

*Dimethoxydiphenylazomethylene*,  $\text{N} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{C}(\text{C}_6\text{H}_4 \cdot \text{OMe})_2$ , m. p. 103–104°.

deep violet crystals, changes in air or in hot benzene to the ketazine, yields tetramethoxytetraphenylethylene when heated with benzene at 150° in an atmosphere of carbon dioxide, and is converted into dimethoxybenzophenone when shaken in benzene in an atmosphere of oxygen. Diphenylazomethylene is converted completely into the ketazine by heat at 150°.

The formation of azomethylenes by the oxidation of the products of the interaction of hydrazine and carbonyl compounds would suggest that these products are hydrazimethylenes. However, against this assumption and in favour of the hydrazone formula are the facts: (i) the azomethylenes cannot be re-converted into hydrazimethylenes by reduction; (ii) the behaviour of the products is easily explained by the hydrazone formula; (iii) almost all of the products are very easily converted into ketazines; (iv) the acetylation of benzylidenehydrazine yields a substance identical with that obtained from acetylhydrazine and benzaldehyde. All hydrazones behave alike when heated, primarily yielding ketazines and hydrazine, by the further interaction of which methane derivatives may be formed; thus the hydrazone of benzil, which gives deoxybenzoin when heated under Curtius's conditions, is converted into bisbenzylketazine at 240°/11 mm. Similarly, fluorenonehydrazone at 200°/18 mm. yields the ketazine (which is converted into fluorene by an excess of hydrazine hydrate at 200°), and dimethoxybenzophenonehydrazone yields bisdimethoxydiphenylketazine at 280°/20 mm., which is converted into dimethoxydiphenylmethane by an excess of hydrazine at 200°. The hydrazone of Michler's ketone yields the ketazine at 280°/14 mm., which is reduced to tetramethyldiaminodiphenylmethane by an excess of hydrazine at 200°. Benzophenone, benzophenoneanil, and benzophenonephenylhydrazone are reduced to diphenylmethane, and benzylideneazine and benzaldehyde to toluene, by an excess of hydrazine at 200°. C. S.

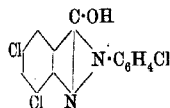
**Synthesis of Iminazole [Glyoxaline] Derivatives.** ADOLF WINDAUS and H. OPITZ (*Ber.*, 1911, 44, 1721–1725. Compare Windaus and Vogt, *Abstr.*, 1907, i, 978).—4-Aminomethylglyoxaline,  $\text{CH}=\text{N} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{C} \cdot \text{CH}_2 \cdot \text{NH}_2$ , is obtained from glyoxaline-4-acetic acid (Knoor, *Abstr.*, 1907, i, 789) by Curtius' method. The *hydrazide*,  $\text{C}_2\text{H}_3\text{ON}_3$ , prepared by boiling ethyl glyoxaline-4-acetate for six hours with a 50% hydrazine hydrate solution, crystallises from absolute alcohol in needles, m. p. 189° (decomp.). The *dihydrochloride* crystallises in prisms insoluble in alcohol, has m. p. 230°, and with amyl nitrite and alcohol yields the urethane, and this when hydrolysed with

concentrated hydrochloric acid gives 4-aminomethylglyoxaline hydrochloride, which crystallises from a mixture of methyl alcohol and ether in long, slender prisms, sintering at 236°.

The *platinichloride*,  $C_4H_6N_2Cl.Pt$ , crystallises in compact, rhombic plates, which decompose at 288°; the *picrate* crystallises from hot water in deep yellow, glistening, six-sided plates, m. p. 209°, and the *picrolonate*,  $C_{24}H_{22}O_{10}N_{11}$ , forms long, yellow needles, m. p. 273° (decomp.).

4- $\beta$ -Hydroxyethylglyoxaline,  $\begin{array}{c} CH=N \\ | \\ NH \cdot CH \end{array} > C \cdot CH_2 \cdot CH_2 \cdot OH$  (?), is obtained by the action of barium nitrite on 4- $\beta$ -aminoethylglyoxaline hydrochloride, and is probably identical with the product formed by the action of yeast on histidine (Ehrlich, this vol., i, 127). The *hydrochloride* crystallises from water in nodular masses of needles; the *platinichloride* forms orange-yellow needles, m. p. 175°, and the *picrolonate* crystallises from alcohol in slender, pale yellow needles, which are much bent, and have m. p. 264° (decomp.). When the hydroxy-compound is treated with 25% nitric acid, the chief product is 5-nitroglyoxaline-4-carboxylic acid,  $\begin{array}{c} CH=N \\ | \\ NH \cdot C(NO_2) \end{array} > C \cdot CO_2H$ , which crystallises from water in long, colourless prisms, m. p. above 300° (decomp.).  
J. J. S.

Hydroxyindazoles. IV. Preparation of Hydroxyindazoles from Non-substituted Benzene-azo- or -hydrazo-benzoic Acids. PAUL FREUNDLER (*Bull. Soc. chim.*, 1911, [iv], 9, 735—739. Compare Abstr., 1903, i, 371, 585; 1904, i, 121, 667, 699; 1906, i, 544; this vol., i, 577).—The method described gives a ready means for preparing unchlorinated or mono-chlorinated hydroxyindazoles, which up to the present have been difficult to obtain. The transformation consists in a simple dehydration, and proceeds more readily when there are more halogen atoms in the benzene nucleus.



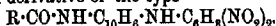
5:7-Dichloro-3-hydroxy-2-p-chlorophenylindazole (annexed formula), white needles, m. p. 209—210°, very sparingly soluble in organic solvents, is prepared by the action of phosphorus pentachloride or thionyl chloride on p-chlorobenzeneazo-o-benzoic acid.

The same method is used for the preparation of several hydroxyindazoles, which have been previously prepared by other methods, and described. 5:7-Dichloro-3-hydroxy-2-phenylindazole can be readily obtained from benzeneazo-o-benzoic acid in this way (compare Abstr., 1907, i, 158).  
W. G.

Ring Formation in the Peri-position in the Naphthalene Series. III. Derivatives of 2':4'-Dinitrophenyl-1:8-naphthylenediamine. FRANZ SACHS and R. B. FORSTER (*Ber.*, 1911, 44, 1738—1748. Compare Abstr., 1909, i, 426).—The condensation of 2':4'-dinitrophenyl-1:8-naphthylenediamine with various acids and carbonyl derivatives has been studied. In the case of



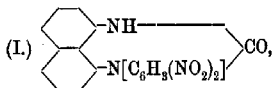
condensing with formic acid, the large, strongly negative dinitro-phenyl group has a retarding effect. With acetic anhydride and most acyl chlorides, ring formation does not occur, the product being a monoacyl derivative of the type



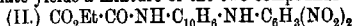
Carbonyl chloride does not condense at all readily with the nitrated base, but ethyl chlorocarbonate yields the *carbethoxy*-derivative,



which gives the cyclic compound 1-*op*-dinitrophenyl-1:3-dihydro-2-perimidone:

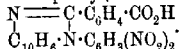


Ethyl oxalate yields a mixture of the two compounds



and (III.)  $\begin{array}{c} N = C \cdot CO_2Et \\ | \\ C_{10}H_6 \cdot N \cdot C_6H_3(NO_2)_2 \end{array}$ , and succinic anhydride reacts in much the same manner.

Condensation with phthalic anhydride takes place readily when a glacial acetic acid solution of the components is boiled for a short time, the product being 1-*op*-dinitrophenylperimidine-2-benzoic acid,



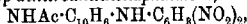
Acetone, ethyl acetoacetate, and other carbonyl derivatives react with the free amino-group only, ring formation does not occur, and products of the type (IV.)  $C_6H_3(NO_2)_2 \cdot NH \cdot C_{10}H_6 \cdot N \cdot CMe_2$  are formed, which are extremely sensitive to acids.

The cyclic perimidine compounds obtained are deeply coloured; their solutions in concentrated sulphuric acid are also coloured, and the colour of the solution is not destroyed by gently heating.

1-*op*-Dinitrophenylperimidine,  $\begin{array}{c} N = CH \\ | \\ C_{10}H_6 \cdot N \cdot C_6H_3(NO_2)_2 \end{array}$ , crystallises

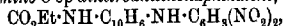
from dilute methyl alcohol in reddish-brown needles, m. p. 175°, and decomposing at 265°. The *picrate*,  $C_{23}H_{13}O_{11}N_7$ , forms orange-red crystals, m. p. 232°.

1-Acetyl-amino-8-*op*-dinitroanilinonaphthalene,



separates from alcohol in yellow crystals, m. p. 237°, and yields a *tetranitro*-derivative, m. p. 248°. The corresponding *benzoyl* derivative,  $COPh \cdot NH \cdot C_{10}H_6 \cdot NH \cdot C_6H_3(NO_2)_2$ , crystallises from glacial acetic acid or xylene, and has m. p. 271—272°, and the *cinnamoyl* derivative,  $CHPh \cdot CH \cdot CO \cdot NH \cdot C_{10}H_6 \cdot NH \cdot C_6H_3(NO_2)_2$ , separates in yellow crystals from xylene, and has m. p. 258—259°.

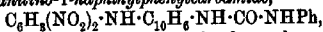
1-Carbethoxylamino-8-*op*-dinitroanilinonaphthalene,



obtained by heating the dinitrated base with ethyl chlorocarbonate at 100° for seventeen hours, forms orange-coloured crystals, m. p. 184—185°, and decomposing at 260—270°. When heated at 193° under 10—12 mm. pressure for 1½ hours, the compound loses ethyl alcohol

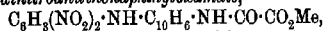
and yields 1-*op*-dinitrophenyl-1:3-dihydro-2-perimidone,  $C_{17}H_{10}O_3N_4$ , which crystallises from xylene in red, triangular prisms, m. p. 267—268° (decomp.), after changing colour at 150°. The crystals contain 0.5 mol. of xylene, which they lose gradually at 100° under reduced pressure.

8-*op*-Dinitroanilino-1-naphthylphenylcarbamide,



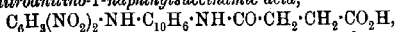
obtained by heating the components in dry xylene, separates from acetic acid in orange-coloured crystals, m. p. 229—230°, and the corresponding thiocarbamide,  $C_{23}H_{17}O_4N_4S$ , obtained by boiling a chloroform solution of the components for twenty-four hours, separates from a mixture of chloroform and light petroleum in glistening, orange-red crystals, m. p. 182°.

Methyl 8-*op*-dinitroanilinonaphthylloxamate,



obtained by heating the dinitro-base with ten times its weight of methyl oxalate for seven days at 100°, crystallises from dilute acetone, and has m. p. 209—210°. The corresponding ethyl ester separates from ethyl acetate in yellow crystals, m. p. 191—192°, and is accompanied by the cyclic compound (III), which forms red crystals, m. p. 171—172°.

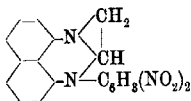
8-*op*-Dinitroanilino-1-naphthylsuccinamic acid,



forms a pale yellow, crystalline powder, turns red at 190°, and decomposes at 227°. When boiled with glacial acetic acid it yields the anhydro-compound,  $C_{20}H_{14}O_3N_4$ , in the form of red crystals sparingly soluble in alcohol and melting at 227°.

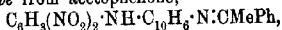
1-*op*-Dinitrophenylperimidine-2-benzoic acid forms yellow crystals, m. p. 297°, and when reduced yields the corresponding diamino-derivative, which is not molten at 340°, although its *picrate* has m. p. 220°.

The dinitro-base reacts with formaldehyde solution in the presence of glacial acetic acid and dilute hydrochloric acid, yielding a compound, probably of the annexed constitution, which decomposes without melting.



8-*op*-Dinitroanilino-1-propylideneamino-naphthalene (IV),

from acetone and the dinitro-base, forms yellow crystals, m. p. 166—167°. The corresponding derivative from acetophenone,

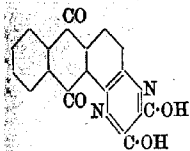


forms red crystals, m. p. 163—164°, and that from ethyl acetoacetate,  $C_6H_3(NO_2)_2 \cdot NH \cdot C_{10}H_6 \cdot N : CMe \cdot CH_2 \cdot CO_2Et$ , has m. p. 167—168°.

J. J. S.

Degradation of Indanthren to Dihydroxypyrazinoanthraquinone and its Behaviour with Benzoyl Chloride and Sodium Ethoxide. ROLAND SCHOLL and SIEGFRIED EDLBACHER (*Ber.*, 1911, 44, 1727—1737. Compare Scholl and Mansfield, *Abstr.*, 1907, i, 255).—Commercial indanthren powder which has been extracted with hydrochloric and glacial acetic acids can be oxidised by

a boiling glacial acetic acid solution of chromium trioxide to  $\alpha\beta$ -dihydroxyanthraquinoxalinequinone ( $\alpha\beta$ -dihydroxy-1:2-pyrazinoanthraquinone) (annexed constitution), which crystallises from nitrobenzene in golden-bronzy needles. It begins to sublime at  $300^\circ$ , and chars at  $370^\circ$ . Boiling sulphuric acid or bromine has no action, and distillation with zinc dust yields anthraquinoxaline. Its sodium derivative,



$C_{16}H_6O_4N_2Br_2$ , obtained by the action of sodium ethoxide, forms a brick-red powder.

Nitrodihydroxyanthraquinoxalinequinone,  $C_{16}H_6O_6N_2$ , obtained by the action of 50% nitric acid, forms a pale yellow powder, and yields a red sodium derivative. The corresponding amino-derivative,



prepared by reducing the nitro-compound with ammonium sulphide, crystallises from nitrobenzene in violet, microscopic needles, m. p.  $365^\circ$ .

$\alpha\beta$ -Dihydroxyanthraquinoxalinequinone can be synthesised by condensing 1:2-diaminoanthraquinone with anhydrous oxalic acid at  $170^\circ$ .

Indanthren yields *N*-benzoyl derivatives (compare Scholl and Berblinger, Abstr., 1907, i, 257) when boiled for an hour with benzoyl chloride or benzoic anhydride. The *dibenzoyl* derivative, *dibenzoyl-N-dihydroanthraquinoneazine* (annexed constitution), crystallises

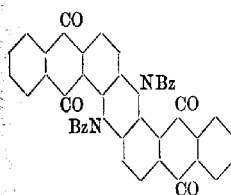
from xylene in red needles, forms an unstable blue additive compound with benzoyl chloride, and is hydrolysed by sulphuric acid or by alcoholic potash to indanthren.

When indanthren is left in contact with a methyl-alcoholic solution of sodium methoxide at the ordinary temperature for twenty-four hours, the colour changes to greyish-green, and, after decanting and washing with methyl alcohol and ether, and finally with absolute ether, a bluish-black sodium compound is obtained. This product is formed by the union of two molecules of sodium methoxide to one of the quinone, probably at the expense of two of the four carbonyl groups originally present. The compound is immediately decomposed by water.

Anthraquinoneazine and sodium methoxide form a green additive compound,  $C_{30}H_{18}O_6N_2Na_2$ , which is completely decomposed by prolonged treatment with methyl alcohol, yielding anthraquinonazhydrine (Abstr., 1904, i, 110). These compounds are analogous to the additive compounds of sodium alkyl oxides with indigocarmin, indigotin, etc.

J. J. S.

Constitution of Alloxantin. M. M. RICHTER (*Ber.*, 1911, 44, 2155—2158).—Piloty and Finckh, and also Slimmer and Stieglitz, have suggested that alloxantin is a combination of alloxan and



dialuric acid resembling the quinhydrone. Since alloxantin does not exhibit the typical criteria (quinonoid structure, colour, easy dissociation) of quinhydrone, the proof of the suggestion is very difficult, and must be limited to the possibility of preparing quinhydrone-like compounds from *p*-benzoquinone and dialuric acid and from quinol and alloxan. The combination of the former pair is impossible, owing to the sensitiveness of dialuric acid to atmospheric oxidation, but a molecular combination of the latter pair has been described by Böhringer & Söhne (1900, D.R.-P. 107720). That the oxygen atom in alloxan can exert a similar, although milder, oxidising action to that of the oxygen in *p*-benzoquinone is shown by mixing concentrated aqueous solutions of alloxan and *p*-phenylenediamine at 30°, whereby is obtained a bluish-black precipitate of *p*-phenylenedi-imine dialurate,  $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{CH} \cdot \text{O} \cdot \text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}$ , the formation of which is explained by the conversion of the *p*-phenylenediamine and the alloxan into *p*-phenylenedi-imine and dialuric acid respectively.

Alloxan and hydrazine hydrate in methyl alcohol yield *alloxan-hydrazine*,  $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{C} \cdot \text{OH} \cdot \text{NH} \cdot \text{NH}_2$  (according to the author's oxonium formula for quinhydrone), a white, amorphous powder, which in the presence of moisture is transformed into *dialurodi-imine*,  $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{CH} \cdot \text{O} \cdot \text{NH}_2 \cdot \text{NH}$ , decomposing rapidly into nitrogen and ammonium dialurate. C. S.

**Benzeneazoxy-*o*-benzoic Acid.** PAUL FREUNDLER (*Bull. Soc. chim.*, 1911, [iv], 9, 739—741).—*Benzeneazoxy-*o*-benzoic acid*,  $\text{O} \begin{smallmatrix} \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H} \\ \text{NPh} \end{smallmatrix}$ , pale yellow spangles, m. p. 110—111°, is prepared by the action of phenylhydroxylamine on *o*-nitrosobenzoic acid in alcoholic solution. It is purified through its barium salt. W. G.

**Hydroxyindazoles. III. Preparation of Ortho-substituted Azo-acids.** PAUL FREUNDLER (*Bull. Soc. chim.*, 1911, [iv], 9, 657—661. Compare this vol., i, 577).—Further condensations of nitrosobenzene with *o*-aminobenzoic esters and of amines with *o*-nitrosobenzoic acids have been effected by the method previously described.

Methyl 5-chloroanthranilate and nitrosobenzene when kept for fifteen days at the ordinary temperature in glacial acetic acid yield a reaction product, from which the following substances can be isolated: (1) the yellow compound,  $\text{C}_{13}\text{H}_{11}\text{O}_3\text{N}_2\text{Cl}$ , m. p. 137°, previously mentioned (*Abstr.*, 1910, i, 446); (2) *methyl 2-benzeneazo-5-chlorobenzoate*, which forms red needles, m. p. 64.5°; (3) the *acid*, of which the yellow compound is the methyl ester; (4) azoxybenzene; (5) *2-benzeneazo-5-chlorobenzoic acid*, which, after purification by the crystallisation of its barium salt, forms orange-red needles, m. p. 126—127°. The barium salt becomes red and anhydrous at 100°.

Yellow bromoanthranilate yields in similar circumstances: (1) a yellow substance; (2) the corresponding acid; (3) azoxybenzene; (4)

*2-benzeneazo-5-bromobenzoic acid*, which crystallises in ruby-red prisms, m. p. 142—143°.

By the interaction of *o*-nitrosobenzoic acid and aniline, benzeneazo-benzoic acid is obtained, and *p*-tolueneazobenzoic acid and *p*-chloro-benzeneazobenzoic acid may be prepared similarly.

*2-Nitroso-m-toluic acid* crystallises in grey prisms, m. p. 172—173° (decomp.). It reacts with *p*-toluidine, yielding *2-p-tolueneazo-m-toluic acid*, which crystallises in large, red prisms, m. p. 122·5°.

*2-p-Tolueneazo-5-chlorobenzoic acid* (from *p*-toluidine and 2-nitroso-5-chlorobenzoic acid) forms orange scales, m. p. 159—160°.

R. V. S.

**Sulphur Linkings in Proteins.** TREAT B. JOHNSON (*J. Biol. Chem.*, 1911, 9, 439—448).—The available evidence on the sulphur linkings in protein is summarised and discussed. It is considered that there are other sulphur combinations besides the cystine group which can break down on hydrolysis with the formation of hydrogen sulphide.

E. F. A.

**Enzyme Action and Electrolytic Dissociation.** HUGO RONKVI (*Biochem. Zeitsch.*, 1911, 34, 176—191).—The differences which have been observed between active and inactivated enzyme solutions are experimentally shown by the author to be due to the evaporation of water during the process of inactivation. The increase in conductivity during the course of the hydrolysis of starch by diastase is shown to be due to the setting free of adsorbed salt molecules. No similar increase is observed when ash-free sucrose is hydrolysed by invertin. On the addition of a substrate to an enzyme solution the changes of the conductivity are quantitatively different when active or inactivated enzyme is used. This change is not specific for the substrate, however, as similar differences are noted when indifferent electrolytes are added to the enzyme solutions. The hydrogen ion concentration in the cases investigated remains unchanged during the digestion process, and there is no difference in the hydrogen ion concentration between active and inactivated enzyme solutions.

S. B. S.

**Action of Ultra-violet Light on Amylase, Invertase, and a Mixture of These Two Diastases.** A. CHAUCHARD and (Mlle.) B. MAZOUÉ (*Compt. rend.*, 1911, 152, 1709—1711).—Malt amylase is much more sensitive to ultra-violet light than the invertase from yeast. It is therefore possible by exposing a mixture of the two to the light from a quartz-mercury lamp to destroy the activity of one before that of the other.

W. O. W.

**The Solubility of the Pancreas Lipase.** L. BERCZELLER (*Biochem. Zeitsch.*, 1911, 34, 170—175).—Experiments with pancreas lipase showed that this enzyme is not soluble either in ether, fats, or fatty acids. The conclusion is drawn that the fat scission by lipase takes place in a heterogeneous system.

S. B. S.

**Enzymic Decomposition of Hydrogen Peroxide.** PERCY WAENTIG and OTTO STECHE (*Zeitsch. physiol. Chem.*, 1911, 72, 226—304. Compare Senter, *Abstr.*, 1905, i, 107; ii, 377).—The decomposition of hydrogen peroxide by the enzymes of blood is not in agreement with a reaction of the first order, nor is it possible to express the course of change by one mathematical expression. There is, however, some proportionality between the enzyme concentration and the amount of hydrogen peroxide decomposed during the first stage of the reaction.

The more highly purified ferment preparations are more susceptible to the adverse influence of impurities. Hydrogen peroxide exerts an adverse influence.

The neutrality or otherwise of the mixture is of great influence on the velocity of reaction, which is quickest at 0° in truly neutral distilled water, and is retarded by the amount of carbon dioxide present in ordinary distilled water or by addition of alkali until indicated by phenolphthalein. At higher temperatures the optimum is in water containing carbon dioxide. When the quantity of acid present is increased, the velocity of change falls at first quickly and later more slowly without the enzyme being damaged. An increase in the amount of alkali decreases the velocity, and the enzyme is also in part destroyed. These changes are more marked at 30° than at 0°.

The influence of an increase of temperature on the rate of change is remarkably small so long as the concentration of the hydrogen peroxide is small.

E. F. A.

**The Reducing Ferments. II. Reduction of Nitrates by the System Perhydrazase, Aldehyde, Water.** ALEXIS BACH (*Biochem. Zeitsch.*, 1911, 33, 282—290).—The author has already suggested that the Schardinger enzyme which reduces methylene-blue is a perhydrazase which acts together with another substance which can be replaced by aldehydes (this vol., i, 412). The reducing action when methylene-blue is replaced by nitrates was then investigated. It was found that fresh milk contains a catalase, which accelerates the reduction of nitrates by aldehydes to such an extent that nitrites could be detected after one or two minutes' action. The increase of both aldehyde and nitrate concentration increases the rate of action, but the increased rate is less than proportional to the increase of the other two constituents of the system. The increased rate of action is, however, proportional to the concentration of the enzyme when the concentration of the other substances is the same. Side by side with the formation of the nitrites, there is a destruction of the latter substance. The optimum temperature is 60—70°. The acetic acid formed in the process has no appreciable action on the rate. In a mixture of milk, nitrite, and aldehyde at 50°, there is a small disappearance of nitrite, which is not sufficient to account for any appreciable loss in the mixture of nitrate, aldehyde, and ferment, and the reason for the small amount of nitrate formed is not yet accounted for in a satisfactory manner. A similar ferment was obtained from the liver of a calf.

S. B. S.

**Preparation of a Nitro-1-aminophenyl-4-arsinic Acid.** FARBERWERKE FORM. MEISTER, LUCIUS & BRÜNING (D.R.P. 232879. Compare this vol., i, 594).—The oxanil-4-arsinic acid previously employed for this preparation can be replaced by *p*-urethanophenylarsinic acid,  $\text{AsO}(\text{OH})_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO}_2\text{Et}$ , needles, decomposing at  $330-340^\circ$ , and obtained by adding ethyl chlorocarbonate to a cooled alkaline solution of *p*-aminophenylarsinic acid. The nitro-compound prepared by nitrating the foregoing urethane in concentrated sulphuric acid solution crystallises from alcohol in yellow needles, and is converted by heating at  $60-80^\circ$  with sulphuric acid into nitro-1-aminophenylarsinic acid. F. M. G. M.

**Quinine Esters of Phenylarsinic Acid Derivatives.** K. J. ORCHSLIN (*Philippine J. Sci.*, 1911, 6, 23-34).—Arsenophenylglycine and atoxyl have been found by Strong and Teague (*Philippine J. Sci.*, 1910, 5, 29) to be the best drugs which have possibilities as a specific against surra; they have the disadvantage, however, that the dose required to effect a cure is too nearly the lethal dose. The author has tested a number of substances (a list of which is given) for their action on trypanosomata, and in the course of the work has prepared the following quinine esters of phenylarsinic acid derivatives.

A suspension of benzoarsinic acid [*p*-carboxyphenylarsinic acid] in dry chloroform is reduced to benzoarsine dichloride by phosphorus trichloride. After evaporation to dryness in a vacuum on the water bath, chloroform and phosphorus pentachloride (1 mol.) are added to the residue, and the resulting solution is treated with quinine in chloroform, whereby ultimately is obtained the quinine ester of benzoarsine dichloride,  $\text{C}_{20}\text{H}_{25}\text{ON}_2 \cdot \text{CO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{AsCl}_2$ . This substance shows an exceedingly high toxicity for trypanosomata *in vitro*, but on the other hand is equally toxic for the cells of the host *in vivo*, and therefore cannot be used therapeutically. It is oxidised by hydrogen peroxide and hydrochloric acid to the quinine ester of benzoarsinic acid,  $\text{C}_{20}\text{H}_{25}\text{ON}_2 \cdot \text{CO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}(\text{OH})_2$ , a heavy, white powder, soluble in acids or alkalis, its solutions in the former being fluorescent.

In a somewhat similar manner, di-*p*-benzoarsinic acid is converted into diquinine dibenzoarsinate,  $\text{C}_{54}\text{H}_{55}\text{O}_8\text{N}_4\text{As}$ , a fine, white powder, and phenylglycinearsinic acid through its acetyl derivative into quinine acetylphenylglycinearsinic acid, a heavy, white powder, which is easily soluble in dilute hydrochloric acid, aqueous ammonia, sodium hydroxide, or sodium carbonate. C. S.

## Organic Chemistry.

**New Catalytic Reaction with Finely Divided Nickel.** H. VAN BERESTEYN (*Bull. Soc. chim. Belg.*, 1911, 25, 293—300).—In attempting to prepare heptyl alcohol from heptaldehyde by the general method of Sabatier and Senderens (compare *Abstr.*, 1905, i, 333), the author, whilst obtaining some of the required alcohol, observed in addition the formation of considerable quantities of *n*-hexylene. This hydrocarbon was also obtained by passing heptyl alcohol over finely divided nickel, in an atmosphere of hydrogen, at 220°, this being the optimum temperature. The reaction is represented by the following equation:  $C_7H_{15}\cdot OH = C_6H_{12} + CH_3\cdot OH$ .

The methyl alcohol formed is decomposed in the reaction into hydrogen and carbon monoxide, the latter being detected in the gaseous products.

W. G.

**Optical Investigation of Argentine Petroleum.** MICHAEL A. RAKUSIN (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 792—793).—Crude Tartahal (Argentine) naphtha is polarimetrically semi-transparent, and the carbonisation constant *K* is greater than 1%, this being in complete correspondence with the small depths of the deposits. Various other specimens of Argentine petroleum were examined.

T. H. P.

**Optical Investigation of Petroleum from Southern Bolivia.** MICHAEL A. RAKUSIN (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 791—792).—Two petroleum from the Yacuiba district of S. Bolivia were found to be virtually optically inactive, and to give no reaction with Tschugaeff's cholesterol reagent, trichloroacetic acid. These properties indicate a modification in the properties of the natural petroleum, as originally formed, by a process of filtration.

T. H. P.

**Presence of Cholesterol in Petroleum.** A. K. KOSS (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 697—707).—The author has made a number of experiments with Ledok and Gogor petroleum (from Java); the results being in disagreement with Engler's view that the optical activity of petroleum is due to a product of the destructive distillation of cholesterol. For instance, when cholesterol was dissolved in a levorotatory fraction of either of these petroleum and the solution completely distilled, the levorotation of the distillate was found to be identical with that of the original fraction. Also, the magnitudes of the levorotations are not altered by treatment of these fractions with ozone.

T. H. P.

**Borislaw Ozokerite.** A. K. KOSS (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 846—855).—Owing to the difficulty of separating the paraffins unchanged from ozokerite by distillation, the author has



used, the extraction method, ether, which dissolves part of the asphaltene and the paraffins of lower boiling point, being used first, and the residue being then extracted with acetone. The portion extracted by the latter is divided into several fractions of varying solubility in acetone. The products were suitably purified before examination. Both the liquid and the solid portions of the ozokerite are found to be free from cholesterol.

If the ozokerite exhibits any optical activity, the active constituents belong exclusively to the liquid portion, boiling at 229—305°/10.5 mm. The rotations observed are very slight and are dextrorotations. The higher the m. p. of the paraffin, the higher is the specific gravity and the lower the degree of unsaturation (iodine number). Also, as the degree of unsaturation of the paraffin fractions diminishes, the dispersion decreases and the refraction increases.

According to Krafft, the specific gravities of normal paraffins at their melting points are almost constant, the value of  $\Delta D$  being very small. With the paraffin fractions under examination, the increase of specific gravity with rise of melting point is much greater than for the normal paraffins, so that isoparaffins are probably present.

T. H. P.

**Fluorobromo-derivatives containing Two Atoms of Carbon.**  
V. FRÉDÉRIC SWARTS (*Bull. Acad. roy. Belg.*, 1911, 563—569. Compare *ibid.*, 1897, 33, 439, and Abstr., 1898, i, 457; 1899, i, 254; 1902, i, 129; 1909, i, 689; 1910, i, 293).—The author has prepared a series of isomeric compounds derived from *as*-tetrabromoethane. A modification of his former method of preparing tribromoethane is given, by which the vinyl bromide formed is separated, collected, and distilled on to the calculated quantity of bromine to give tribromoethane. This is then converted into *as*-dibromoethylene by boiling in alcoholic solution with potassium carbonate and potassium acetate for thirty-six hours. The resulting product after distillation out of contact with air gives on bromination the required *as*-tetrabromoethane, b. p. 112.5°/18 mm. The action of antimony fluoride on this substance is similar to that on bromoform, but is markedly different from that on either *s*-tetrabromoethane or tribromoethane. The reaction with antimony fluoride is somewhat complex. By using  $\frac{1}{3}$  mol. of this reagent for every mol. of tetrabromoethane, working at 135°, the principal product is fluorotribromoethane. The other products of the reaction are tetrabromoethylene, and a liquid, b. p. 206—209°, which appeared to be fluorotetrabromoethane.

By using  $\frac{2}{3}$  mol. antimony fluoride the principal product is difluorodibromoethane,  $\text{CF}_2\text{Br}\cdot\text{CH}_2\text{Br}$ . The other products are trifluorobromoethane, difluorotribromoethane, pentabromoethane, fluorotetrabromoethane, and tetrabromoethylene.

$\alpha$ -Fluoro- $\alpha\beta$ -tribromoethane (Abstr., 1909, i, 690) is a colourless liquid, b. p. 162.7°/757 mm.,  $D_{17}^{25}$  2.6054,  $n_D^{17}$  1.50215; when acted on by potassium ethoxide in an atmosphere of hydrogen, it yields  $\alpha$ -fluoro- $\alpha\beta$ -dibromoethylene,  $\text{CFBr}\cdot\text{CHBr}$ , b. p. 88.8°,  $D_{17}^{25}$  2.2890. On leading oxygen into this substance, *dibromoacetyl fluoride* is produced. Alcohol decomposes this, giving ethyl dibromoacetate.

Another method is given for the preparation of fluorobromoethylene (compare *Bull. Acad. roy. Belg.*, 1909, 709) by the action of zinc dust on fluorotribromoethane. The whole operation is conducted in the absence of air, and the product so obtained has b. p.  $6.8^{\circ}$ , and can be kept in a sealed tube without showing any signs of alteration after eighteen months.

*aa-Difluoro- $\beta$ -bromoethylene*,  $\text{CF}_2\text{CHBr}$ , is obtained by boiling an alcoholic solution of difluorodibromoethane with potassium carbonate and potassium acetate. It is a colourless liquid, b. p.  $6.2^{\circ}$ ,  $D_4^{20}$  1.82, and is not acted on by air.

*Difluorobromodiethyl ether*,  $\text{CF}_2\text{Br}\cdot\text{CH}_2\cdot\text{OEt}$ , obtained by the action of sodium ethoxide on difluorodibromoethane, is a colourless liquid with a pungent odour, b. p.  $114-115^{\circ}$ , which on oxidation with nitric acid yields bromoacetic and hydrofluoric acids.

*a-Fluoro- $\alpha\beta\beta$ -tetrabromoethane*,  $\text{CFBr}_3\cdot\text{CHBr}_2$ , a colourless liquid, b. p.  $211^{\circ}$ , or  $106.4^{\circ}/24$  mm.,  $D_4^{20}$  2.9094, results from the action of bromine on the above fluorodibromoethylene.

*aa-Difluoro- $\alpha\beta\beta$ -tribromoethane*,  $\text{CF}_2\text{Br}\cdot\text{CHBr}_2$ , a colourless liquid, b. p.  $143.4-143.5^{\circ}/754$  mm.,  $D_4^{20}$  2.60769,  $n_D^{20}$  1.50215, is obtained by the bromination of *aa*-difluoro- $\beta$ -bromoethylene. On treatment with potassium ethoxide in an atmosphere of nitrogen, it yields *difluorodibromodiethyl ether*,  $\text{CHBr}_2\cdot\text{CF}_2\cdot\text{OEt}$ , a mobile liquid, b. p.  $67.2^{\circ}/25$  mm.,  $D_4^{20}$  1.9158, giving with nitric acid, hydrofluoric and dibromoacetic acids.

The author attempted to prepare a tetra-substituted ethylene by the action of potassium carbonate and potassium acetate on difluorotribromoethane. The greater portion of the product was the above ether, and only a small amount of *aa*-difluoro- $\beta\beta$ -dibromoethylene was obtained, which, being difficult to purify, was brominated, giving *aa*-difluoro- $\alpha\beta\beta$ -tetrabromoethane,  $\text{CF}_2\text{Br}\cdot\text{CBr}_3$ , a solid, m. p.  $99^{\circ}$ , b. p.  $185^{\circ}$ , having a camphor-like odour. A mixture of antimony fluoride and bromine had practically no action on it.

*$\alpha\beta$ -Trifluoro- $\beta$ -bromoethane*, one of the by-products in the action of antimony fluoride ( $\frac{2}{3}$  mol.) on tetrabromoethane, is obtained by the action of silver fluoride on *aa*-difluoro- $\alpha\beta$ -dibromoethane in sealed tubes at  $120^{\circ}$ , as a liquid, b. p.  $24.8-25^{\circ}$ . It does not react with either mercuric oxide and water at  $130^{\circ}$ , or with potassium ethoxide at  $40^{\circ}$ . When treated with sodium methoxide at  $150^{\circ}$  for seven hours, it gives *methyl trifluoroethyl ether*,  $\text{CH}_3\text{F}\cdot\text{CF}_2\cdot\text{OMe}$ , b. p.  $45^{\circ}$ .

The group  $\cdot\text{CF}_2$  imparts inertia to the molecule, as is shown by the fact that, whereas  *$\alpha\beta$ -difluoro- $\alpha\beta\beta$ -tribromoethane*,  $\text{CFBr}_2\cdot\text{CHBrBr}$ , can be fluorinated, the corresponding  *$\alpha\alpha\beta$ -trifluoro- $\alpha\beta$ -dibromoethane*,  $\text{CF}_2\text{Br}\cdot\text{CHFBr}$ , cannot be so acted on. Similarly, the bromine atom in the chain  $\cdot\text{CF}_2\text{Br}$  has very little mobility, and cannot be displaced by potassium ethoxide.

Further, in the ethylenes this group  $\cdot\text{CF}_2$  gives stability. The compounds  $\text{CF}_2\cdot\text{CH}_2$  and  $\text{CF}_2\cdot\text{CHBr}$  do not undergo oxidation in air, whilst the compounds  $\text{CBr}_2\cdot\text{CH}_2$  and  $\text{CBrBr}\cdot\text{CHF}$  are oxidised readily. On the other hand, the group  $\cdot\text{CFBr}$  seems the most reactive towards oxygen, and in the compound  $\text{CF}_2\cdot\text{CFBr}$ , the group  $\cdot\text{CF}_2$  cannot inhibit the oxidising action on the group  $\cdot\text{CFBr}$ .

If the general structure of the molecule remains unaltered, the transposition of fluorine and bromine atoms has little or no effect on the b. p. and density of the compound.

W. G.

**Action of Some Organic Acids on Sodium Formate.** WILLIAM OESCHNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1911, 440—442).—By the dry distillation of sodium formate mixed with either malonic, succinic, or tartaric acids in the requisite molecular proportions, formic acid passes over, and may be recognised by its reducing power or by the formation of ethyl formate. Tartaric acid is the least active of the three acids, and, in the case of malonic acid, acetic acid can also be found in the distillate.

W. G.

**Action of Some Organic Acids on Sodium Formate.** II. WILLIAM OESCHNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1911, 590—591. Compare preceding abstract).—Benzoic and tannic acids readily, gallic acid moderately, the three isomeric hydroxybenzoic acids and cinnamic acid feebly, *p*-nitrobenzoic acid partly, if the operation is carefully conducted, and malic acid only partly, displace formic acid from sodium formate on dry distillation.

Incidentally the author notes certain points as to the behaviour of cinnamic acid on sublimation and dissolution, and mentions ethyl alcohol or pure methyl alcohol as the best solvents for it.

W. G.

**The Optically Active Modifications of Lactic Acid.** REGINALD O. HERZOG and P. SLANSKY (*Zeitsch. physiol. Chem.*, 1911, 73, 240—246).—Jungfleisch (Abstr., 1904, i, 645) has stated that the two optically active modifications of lactic acid are racemised in alkaline solution at different rates. The two modifications have now been prepared with the aid of morphine by Irvine's method (*Trans.*, 1906, 89, 935), and heated both in alkaline acid and neutral solution. The rotations were determined in presence of ammonium molybdate under standard conditions. No difference whatever was found in the behaviour of the two antipodes.

E. F. A.

**Electrolytic Reduction of Lævulic Acid and  $\alpha$ -Dimethyl lævulic Acid.** JULIUS TAFEL and BRUNO EMMERT (*Zeitsch. Elektrochem.*, 1911, 17, 569—572).—Alkaline solutions of the acids were reduced at a prepared lead cathode at about 20° with a current density of about 0.12 ampere per sq. cm. (Abstr., 1900, ii, 588). With acid solutions, it was necessary to add alcohol in order to prevent the formation of a non-conducting film of valeric acid on the lead cathode, or else to use a cathode of mercury instead of lead.

Lævulic and dimethyl-lævulic acid are reduced in alkaline solutions to the corresponding hydroxy-acids or lactones.

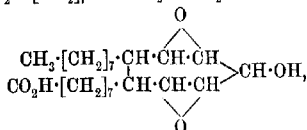
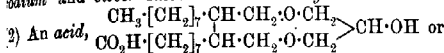
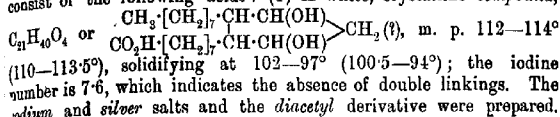
In acid solutions lævulic acid is reduced to valeric acid, but dimethyl-lævulic acid yields the corresponding lactone as the principal product, only small quantities of dimethylvaleric acid being formed.

Hydroxyvaleric acid, valerolactone, and  $\alpha$ -dimethylvalerolactones are not reduced at all under the conditions used, and these substances cannot therefore be regarded as intermediate products in the reduction to the fatty acids.

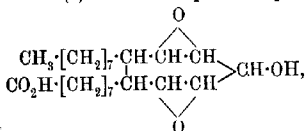
T. E.

**Reactions of Certain Unsaturated Fatty Acids with Formaldehyde.** SERGIUS FORIN (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 809—819).—The author has studied the compounds obtained by the condensation of oleic, elaidic, and undecolic acids with formaldehyde in presence of sulphuric acid. It is found that more definite and non-polymerised products are obtained if the reaction is carried out at low temperatures.

With oleic and elaidic acids the products seem to be identical, and consist of the following acids: (1) A white, crystalline compound,

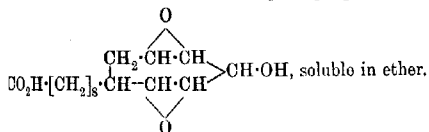


which was obtained as a liquid soluble in light petroleum, and forms a monoacetyl derivative. (3) A viscous liquid acid, probably



having a bitter taste; it is insoluble in light petroleum, and forms a monoacetyl derivative. The sodium salt was analysed.

In the case of undecolic acid the principal product is a viscous liquid,



T. H. P.

**The Hæmolytic Action of the Fat of Rice (*Oryza sativa*, L.)**  
**Hæmolysis of Fatty Acids.** J. SHIMAZONO (*Arch. exp. Path. Pharm.*, 1911, 65, 361—366).—The alcoholic and ethereal extracts of rice possess hæmolytic properties which the author traced to the palmitic acid present. This observation led him to study the hæmolytic powers of other fatty acids; working upwards from formic acid, these properties were absent in the lower members, and did not appear until nonoic acid was reached. The higher acids were markedly hæmolytic. It thus appears possible that the hæmolytic

action of various organs vaguely ascribed to lipoids, etc., may in reality be due to higher fatty acids.

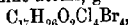
E. J. R.

**Cochineal Fat.** R. HUERRE (*J. Pharm. Chim.*, 1911, [vii], 4, 56—65).—The fat extracted by boiling ether from "silver cochineal" has m. p. 32°, iodine number 50.53, and the percentage composition free fatty acids 89, glycerides 8, and unsaponifiable matter 3. Liebermann has shown already that the saturated acid present is myristic, and the author finds that the liquid acids are composed of oleic 35% and linoleic 8%, calculated on the "total fatty acids." Oleic acid was isolated by means of the lead salt, but attempts to isolate the linoleic acid in a pure state by Farnsteiner's method (Abstr., 1899, ii, 705) and by the process Haller has used for the separation of oleic acid from saturated fatty acids (Abstr., 1907, i, 9, 10) were unsuccessful, and the presence of linoleic acid was proved by the detection of tetrahydroxystearic acid in the products of oxidation of the liquid fatty acids by permanganate. The unsaponifiable matter is orange-coloured, and has a high iodine number.

T. A. H.

**Fatty Acids of Cod-liver Oil.** ALFRED HEIDUSCHKA and E. RHEINBERGER (*Pharm. Zentr.-h.*, 1911, 52, 837—838).—It has been shown previously that the fatty acids of cod-liver oil on treatment with Hübl's iodine solution furnish a crystalline derivative,  $C_{17}H_{33}O_2Cl_4$ , of terapic acid,  $C_{17}H_{33}O_2$ , in which the iodine can be replaced by chlorine, forming terapic acid octachloride (Abstr., 1910, i, 297).

The first of these derivatives on treatment with zinc and acetic acid furnishes an acid,  $C_{17}H_{33}O_2$ , as a nearly colourless oil, distilling at 154°/75 mm., and having iodine number 264.5. When terapic acid tetrachloride tetraiodide is treated with bromine, the four iodine atoms are replaced by bromine atoms, giving the compound,



m. p. 150°, which forms a yellowish-brown, crystalline powder, soluble in the usual organic solvents.

Terapic acid octachloride forms a potassium salt. *Linolenic acid trichloride triiodide*,  $C_{18}H_{31}O_2Cl_3I_3$ , m. p. 95°, formed by the action of Hübl's iodine solution on the mixed fatty acids of linseed oil, is a colourless, crystalline substance, soluble in alcohol or chloroform.

T. A. H.

**Soya Bean Oil.** S. KEIMATSU (*Chem. Zeit.*, 1911, 35, 839—840).—The oil used had the following constants:  $D_{20}^{20}$  0.9265, viscosity at 20° 8.9 to 9.0 (Engler's apparatus), solidifying point  $-15^\circ$  to  $-16^\circ$ , m. p.  $-7^\circ$  to  $-8^\circ$ , solidifying point of fatty acids  $16^\circ$ — $17^\circ$ , m. p. of fatty acids 23— $24^\circ$ , saponification number 190, iodine value 132—135, and Hehner number 94.2. It contained 0.2% of a phytosterol, m. p.  $136^\circ$ — $137^\circ$ , which was not stigmasterol. The fatty acids were separated into saturated and unsaturated by means of the lead salts. The former included palmitic and stearic acids (together 12%). The unsaturated acids on oxidation furnished isolinolic, dihydroxystearic, and sativic acids, together with an isomeride of sativic acid, m. p.  $168^\circ$ — $169^\circ$  (compare Hartley, Abstr., 1909, ii, 597), and an unidentified

acid, m. p. 145—149°, probably impure.\* These oxidation products indicate the presence in the oil of the following acids, isolinolenic, oleic, linoleic (these two together 15%), and an isomeride of linoleic acid (50%).

T. A. H.

**Preparation of Oxalic Acid by the Fusion of Sawdust with Potassium Hydroxide.** A. VON HEDENSTRÖM (*Chem. Zeit.*, 1911, 35, 853—854).—There being no exact details as to yields, temperature of fusion, etc., in the manufacture of oxalic acid from sawdust, the author has\*carried out the following experiments, using, in the preliminary work, purified cotton wool instead of sawdust.

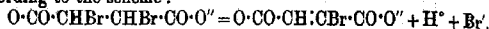
Three grams of cotton-wool were heated with 12 grams of potassium hydroxide and 20 c.c. of water in a nickel crucible on a sand-bath, the temperature of the mass being carefully taken. The best yield, 3.72 grams of oxalic acid, was obtained when the temperature was gradually raised to, and maintained at, 280° until no further reaction took place, the fusion then being cooled with continuous stirring. The yield is much less, 1 gram, when the temperature does not exceed 225°, even on prolonged heating. The addition of potassium oxalate in small quantity, as also of potassium permanganate or lead peroxide, further increases the yield of oxalic acid at 280°; the passage of air through the fusion has a similar effect.

Three grams of oak sawdust gave similar results and yields to the cotton-wool. It is thus probable that the lignin substances give oxalic acid as well as the cellulose, and this was confirmed by first extracting the sawdust with a 10% solution of potassium hydroxide at the ordinary temperature, filtering, evaporating the filtrate to dryness, and fusing the residue at 280°. 1.27 Grams of oxalic acid were obtained, which, together with 2.36 grams of oxalic acid obtained from the residual sawdust after extraction, give 3.63 grams, which is practically the same yield as 3.66 grams obtained by direct fusion of 3 grams of sawdust. No oxalic acid was obtained by the extraction of cotton-wool with 10% potassium hydroxide.

T. S. P.

**Stereoisomeric Dihalogensuccinic Acids.** BROR HOLMBERG (*J. pr. Chem.*, 1911, [ii], 84, 145—168).—The author has measured the velocity of decomposition of dibromosuccinic, isodibromosuccinic, dichlorosuccinic, and isodichlorosuccinic acids, and also of their normal and acid barium salts in (1/30 molar) aqueous solution at 25°, by determining the increase of acidity by means of standard alkali, and finds that the reactions are all of the unimolecular type. The close agreement in the values obtained for the velocity constants indicates that the decomposition of the acids is not affected by the presence of the halogen acid formed in the reaction, and this is confirmed by the comparatively small differences in the constants, obtained for the decomposition of one and the same acid (1) in aqueous solution, (2) in the presence of hydrochloric acid, (3) in the form of its barium hydrogen salt. Although Lossen and Reisch (*Abstr.*, 1898, i, 357) have shown that several reactions take place simultaneously during the decomposition of dibromosuccinic acid in aqueous solution, under

the conditions chosen by the author the decomposition occurs mainly according to the scheme:



The behaviour of the isomeric dibromosuccinic acids towards potassium sulphide, potassium xanthate, sodium ethyl sulphide, and potassium trithiocarbonate has also been investigated. When dibromosuccinic acid, in the form of its sodium salt, is allowed to react with these substances in aqueous solution, it is almost quantitatively transformed into fumaric acid, whilst the *iso*-acid, under the same conditions, reacts with difficulty, yielding mainly bromofumaric acid. \*

Measurements have also been made of the electrical conductivity of the acids and their sodium hydrogen salts, and also of the hydrogen-ion concentration of the same substances in aqueous solution by Bredig and Fraenkel's method (Abstr., 1905, ii, 692); from the results thus obtained, the following values for the primary ( $k$ ) and secondary ( $s$ ) affinity constants of the acids have been calculated: dichlorosuccinic acid,  $k=0\cdot03$ ,  $s=8\cdot1$ ; isodichlorosuccinic acid,  $k=0\cdot035$ ,  $s=9\cdot9$ ; dibromosuccinic acid,  $k=0\cdot037$ ,  $s=13\cdot6$ ; isodibromosuccinic acid,  $k=0\cdot37$ ,  $s=4\cdot3$ .

Unsuccessful attempts to resolve dibromosuccinic acid by crystallisation of the alkaloidal salts are recorded.

The cinchonine salt,  $\text{C}_{42}\text{H}_{45}\text{O}_6\text{N}_4\text{Br}_2\cdot6\text{H}_2\text{O}$ , and strychnine salt,  $\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2\cdot\text{C}_4\text{H}_4\text{O}_4\text{Br}_2$ ,

are described.

F. B.

**Formation of Cork.** S. ZEISEL (*J. pr. Chem.*, 1911, [iii], 84, 317—323).—The author criticises adversely the work of Schmidt (Abstr., 1910, i, 540) on this subject, and maintains that the latter's experiments lend no support to the view that cork is produced by the formation of anhydrides and polymerisation of fatty acids, originally present in young cork in the form of glycerides.

F. B.

**Sulpho-etheral Salts or Thionic Esters,  $\text{R}\cdot\text{CS}\cdot\text{OR}$ .** MARCEL DELÉPINE (*Compt. rend.*, 1911, 153, 279—282. Compare Abstr., 1910, i, 295).—The following thionic esters have been prepared by the method already indicated (Abstr., 1910, i, 612), or by Matsui's process (Abstr., 1909, i, 463). Experimental details are given for the former.

Ethyl thionacetate,  $\text{CH}_3\cdot\text{CS}\cdot\text{OEt}$ , b. p.  $109\text{--}110^\circ$ ,  $D_4^{20} 0\cdot9816$ . Ethyl thionpropionate, b. p.  $130\text{--}132^\circ$ ,  $D_4^{20} 0\cdot9639$ . Methyl thionisobutyrate, b. p.  $145\text{--}148^\circ$ ,  $D_4^{20} 0\cdot9577$ ; the ethyl ester has b. p.  $169\text{--}165^\circ$ ,  $D_4^{20} 0\cdot9549$ . Methyl thionisovalerate, b. p.  $160\text{--}170^\circ$  (l). Methyl thionooctate, b. p.  $115\text{--}120^\circ/12$  mm. Methyl thionbenzoate, b. p.  $110\text{--}112^\circ/10$  mm. Methyl thioncyclohexoate, b. p.  $90\text{--}100^\circ/12$  mm. The last four compounds were not obtained perfectly pure.

The methyl and ethyl esters fume in the air, are strongly phosphorescent, and have an ozone-like odour up to the  $\text{C}_8$  terms. The thionbenzoates are also phosphorescent. The higher members of the series as well as the hydroaromatic compounds do not show these properties.

W. O. W.

**Photochemical Synthesis of Carbohydrates in Absence of Chlorophyll.** JULIUS STOKLASA and VENCESLAS ZDOBNICKY (*Bull. Assoc. Chim. Sucr. Dist.*, 1911, 29, 26—31).—In presence of potassium hydroxide, carbon dioxide and nascent hydrogen interact with production of formic acid. Under the influence of ultra-violet rays a sugar is formed.

Formaldehyde is produced by the interaction of water vapour and carbon dioxide in presence of potassium hydroxide and ultra-violet rays.

Negative results were obtained by submitting (1) water vapour and carbon dioxide, and (2) carbon dioxide, nascent hydrogen, and potassium hydroxide to the action of ultra-violet rays. N. H. J. M.

**Instability of Dextrose at the Temperature and Alkalinity of the Body.** LAWRENCE J. HENDERSON (*J. Biol. Chem.*, 1911, 10, 3—7).—It is suggested that the very exact regulation of the alkalinity of the body has as one of its principal objects the preservation of a suitable medium for the destruction of dextrose and the regulation of the process. When dextrose is boiled with a mixture of sodium hydrogen phosphate and disodium hydrogen phosphate in varying proportions, the mixture becomes optically inactive within a few hours. Similar solutions preserved with toluene in sealed flasks at 38° for forty-four days showed a slight loss in optical activity.

E. F. A.

**Action of Sodium and Potassium Hydroxides on the Optical Behaviour of Dextrose in Solution.** S. C. PROFILO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1911, [iii], 17, 174—181).—In the presence of a fairly high concentration of sodium or potassium hydroxide, a solution of dextrose, which is at first dextrorotatory, slowly diminishes in optical activity and becomes levorotatory; after a long interval, the levorotation has diminished to such an extent that the solution is optically neutral. It is suggested that an equilibrium mixture of dextrose, levulose, and mannose is finally formed, represented by the equation: dextrose  $\rightleftharpoons$  levulose  $\rightleftharpoons$  mannose, and that the sign of the rotation depends on the relative proportions of these substances present. It is possible that after a time the mixture would again become dextrorotatory, but readings ultimately become impossible owing to the depth of colour of the solution. G. S.

**Behaviour of Sucrose and its Decomposition Products on Heating.** J. E. DUSCHSKY (*Zeitsch. Ver. deut. Zuckerind.*, 1911, 855—879. Compare this vol., i, 607).—Concentrated sucrose solutions of alkaline reaction withstand heating at temperatures up to 130° without appreciable decomposition, as measured either by a fall in the polarisation or by the formation of reducing substances. In cases where a change does take place in solutions which were originally alkaline, it is found that the alkalinity has been destroyed by acid decomposition products, which subsequently facilitate a complete decomposition. Excess of alkali and the nature of the alkali have no influence on the decomposition of concentrated sucrose solutions.

When the reaction is acid, decomposition ensues without any



regularity, and its amount is not proportional to the time or temperature of heating. At first dextrose and levulose are formed, and these are further changed to a series of optically active and inactive substances.

Both in concentrated and in dilute solution the decomposition of sucrose is facilitated before all by the reaction of the medium, and then by the temperature and period of heating. The influence of concentration is subordinate and very irregular.

The quantitative results of heating sucrose solutions of alkaline reaction of 50% to 75% concentration for one hour at temperatures from 80° to 135° are contained in a series of tables which give the amount of sugar lost by the process. Heating has but little influence up to 110°; at higher temperatures the loss increases rapidly, amounting to 0.2% to 0.3% at 120°. This indicates that it is inadvisable to warm sugar solutions above a certain limit, and the determinations of the destruction of alkali on heating, which are also tabulated, point to the same conclusion.

E. F. A.

**Empirical Relation between the Configuration and Rotation of Sugars.** ERNEST ANDERSON (*J. Amer. Chem. Soc.*, 1911, 33, 1510—1514).—The direction and degree of optical rotation of the sugars are determined by the configuration of the  $\alpha$ - and  $\beta$ -carbon atoms. The four possible configurations with their corresponding rotations are:

OH H	
$\cdot\text{C}—\text{C}\cdot\text{CHO}$	= strongly dextrorotatory.
H OH	
H OH	
$\cdot\text{C}—\text{C}\cdot\text{CHO}$	= strongly levorotatory.
OH H	
OH OH	
$\cdot\text{C}—\text{C}\cdot\text{CHO}$	= slightly dextro- or levo-rotatory.
H H	
H H	
$\cdot\text{C}—\text{C}\cdot\text{CHO}$	= slightly dextro- or levo-rotatory.
OH OH	

It is claimed that this applies to all sugars for which both configuration and rotation are known. The theory is applied to the determination of configuration when the rotatory power is known.

E. F. A.

**Action of Oxalic and Malonic Acids on Starch and Dextrin.** WILLIAM OECHSNER DE CONINCK and A. RAYNAUD (*Bull. Acad. roy. Belg.*, 1911, 438—439. Compare this vol., i, 423, 607).—With these two dibasic acids the amount of hydrolysis is proportional to the concentration of the acids, and the quantity of dextrin hydrolysed is always greater than that of starch hydrolysed. In the latter respect the two acids under consideration resemble the mineral acids already studied, and differ from the monobasic formic and acetic acids.

W. G.

**Action of Lactic and Tartaric Acids on Starch and Dextrin.** WILLIAM OCHSENER DE CONINCK and A. RAYNAUD (*Bull. Acad. roy. Belg.*, 1911, 592—593. Compare this vol., i, 423, 617, and preceding abstract).—In the case of these two hydroxy-acids the rates of hydrolysis for starch and dextrin are practically the same, the two acids thus resembling formic and acetic acids in their behaviour.

The conclusion drawn from the whole series of experiments is that the rate of saccharification, per molecule of acid, is three or four times greater with mineral than with organic acids. W. G.

**New Solvents for Cellulose and their Action on this Substance.** HORACE G. DEMING (*J. Amer. Chem. Soc.*, 1911, 33, 1512—1525).—Cellulose in the form of filter paper is soluble in concentrated aqueous solutions of antimony trichloride, stannous chloride, and zinc bromide. When dissolved in the halogen acids (hydrochloric acid, etc.), these salts and many others dissolve cellulose with great ease. A few salts in solution in formic or trichloroacetic acids also act as solvents for cellulose.

Cellulose attracts metallic salts in solution, forming an adsorption complex, and the salt is distributed between the fibre and the solution. When an agent is present which, like certain dilute acids, can bring about union with water, the complex is brought into solution.

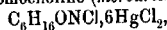
In proof of this view much evidence is adduced. Cellulose modified by acids becomes soluble in aqueous calcium chloride solutions which cannot dissolve pure cellulose. Chlorosulphonic, arsenic, and selenic acids are able to dissolve cellulose.

Celluloses dissolved in acid solutions of salts are precipitated on pouring into water as amorphous compounds with marked reducing properties and easily hydrolysed.

One of the formates of cellulose when hydrolysed by concentrated hydrochloric acid is converted into compounds soluble in water, and finally into dextrose. E. F. A.

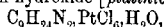
**$\beta$ -Aminoethyl Alcohol, a Product of the Hydrolysis of the Lecithin of Bean Meal.** GEORG TRIER (*Zeitsch. physiol. Chem.*, 1911, 73, 383—388).— $\beta$ -Aminoethyl alcohol is obtained among the products of the hydrolysis of the phosphatide of bean meal (*Phaseolus vulgaris*) with barium hydroxide, and proved to be in all respects identical with the synthetic product.  $\beta$ -Aminoethyl alcohol is regarded as the parent substance of choline, which is evidently derived from it by complete methylation in the plant. E. F. A.

**Homocholine and Neosine.** E. BERLIN (*Zeitsch. Biol.*, 1911, 57, 1—74).—The chief point of chemical interest is a comparison of the homocholines obtained by various investigators. The author decides that Malengreau and Lebailly's  $\beta$ -homocholine (*Abstr.*, 1910, i, 545) is identical with Morley's (*Abstr.*, 1881, 151; Morley and Green, *Ber.*, 1885, 18, 24), and that the constitution  $\text{OH} \cdot \text{NMe}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$  of Weiss' (*Zeitsch. Naturwiss.*, 1887, 60, 221) and of Schmidt and Partheil's (*Abstr.*, 1892, 950)  $\gamma$ -homocholine is not proved. The author has prepared  $\gamma$ -homocholine (mercurichloride,



m. p. 208°; *picrate*, m. p. 255°) by the same method as Malengreau and Lebailly (*loc. cit.*), and has proved its constitution by oxidising it to  $\beta$ -homobetaine by calcium or barium permanganate and warm dilute sulphuric acid. He finds that its aurichloride has m. p. 193—194°, whereas Malengreau and Lebailly give 183°. In consequence of this discrepancy, the author prepares  $\gamma$ -homocholine by another process, and has thereby cleared away much of the confusion in the literature of the homocholines. By exhaustive methylation,  $\gamma$ -aminopropyl alcohol yields two homocholines, which are separated best by means of their mercurichlorides. The less soluble fraction, m. p. 203°, of the mercurichlorides yields an aurichloride, m. p. 187—190°, the base in which is proved to be  $\gamma$ -homocholine by its oxidation to  $\beta$ -homobetaine. The more soluble fraction, m. p. 208°, of the mercurichlorides yields an aurichloride, m. p. 163° [the same as that of Weiss' and of Schmidt and Partheil's  $\gamma$ -homocholine aurichloride (*loc. cit.*)], the base in which is proved to be  $\beta$ -homocholine by its oxidation to betaine. Consequently the so-called  $\gamma$ -homocholine of these two investigators is in reality  $\beta$ -homocholine. A feasible explanation is given for the production of  $\beta$ -homocholine in Schmidt and Partheil's method, and also in the author's second process (above). A discrepancy, as yet unexplained, still remains; Malengreau and Lebailly (*loc. cit.*) give the m. p. of  $\beta$ -homocholine aurichloride as 195—196°.

By-products in the preparation of  $\gamma$ -homocholine from trimethylamine and trimethylene chlorohydrin are the ether of  $\gamma$ -homocholine [*platinichloride*,  $O(CH_2 \cdot CH_2 \cdot CH_2 \cdot NMe_3)_2 \cdot PtCl_6$ , m. p. 253—254°, *aurichloride*,  $C_{12}H_{30}ON_3 \cdot 2AuCl_4$ , m. p. 230—232°] and hexamethyltrimethylenediammonium hydroxide [*platinichloride*,



m. p. 258—260° (decomp.)]; the latter is also formed in the author's second process.

Neosine has been isolated from shrimps by Kutscher and Ackermann's method (Abstr., 1908, i, 675). It contains choline, the removal of which is very difficult, but sufficient pure material has been obtained to show, by a comparison of the platinichlorides, mercurichlorides, and aurichlorides, that neosine is not identical with  $\gamma$ -homocholine (compare Kutscher and Ackermann, *loc. cit.*).

Two points of physiological interest are discussed. Firstly, it is shown that  $\gamma$ -homocholine chloride is decidedly more poisonous than choline chloride; thus is disproved Meyer and Schmidt's statement (Abstr., 1905, i, 23) that the physiological activity of the base is weakened when the side-chain is lengthened. Secondly, there has been a controversy as to whether the lowering of the blood-pressure by the injection of choline chloride is due to the substance itself or to an impurity therein. The former view is supported by the author's experiments, since synthetic choline chloride,  $\gamma$ -homocholine chloride, and  $\beta$ -homocholine chloride (in which the presence of such an impurity is almost impossible) all cause a lowering of the blood-pressure. It is remarkable that  $\gamma$ -homocholine ether and hexamethyltrimethylenediammonium dichloride are, comparatively, non-poisonous.

C. S.

**d- $\alpha$ -Aminobutyric Acid and l- $\alpha$ -Aminobutyrylglycine.** ARTHUR H. KOELKER (*Zeitsch. physiol. Chem.*, 1911, 73, 312—313).—*r*- $\alpha$ -Aminobutyrylglycine has been asymmetrically hydrolysed by means of an active enzyme in yeast into d- $\alpha$ -aminobutyric acid,  $[\alpha]_D^{20} + 9^\circ$ , glycine, and l- $\alpha$ -aminobutyrylglycine,  $[\alpha]_D^{20} - 86.4^\circ$ .  
E. F. A.

**Production of Some Amino-acids from the Phenylhydrazones of Ketonic Acids by Aluminium Amalgam, and Preparation of the Optically Active  $\gamma$ -Aminovaleric Acids.** EMIL FISCHER and REINHART GROH (*Annalen*, 1911, 383, 363—372).

—When reduced in alcoholic solution by aluminium amalgam and water, the phenylhydrazones of lævulinic acid, ethyl acetoacetate, and pyruvic acid yield  $\gamma$ -aminovaleric acid,  $\beta$ -aminobutyric acid (best method of preparation), and alanine respectively in 55—60% yield.

*r*- $\gamma$ -Aminovaleric acid, in the form of its benzoyl derivative, is easily resolved by quinine. d- $\gamma$ -Benzoylaminovaleric acid,  $C_{12}H_{15}O_5N$ , has m. p.  $133^\circ$  (corr.),  $[\alpha]_D^{20} - 21.9^\circ$  in alcohol, and is less soluble in water than the racemic form. When hydrolysed by 20% hydrochloric acid on the water-bath, it yields d- $\gamma$ -aminovaleric acid, m. p.  $214^\circ$  (corr., decomp.), and  $[\alpha]_D^{20} 12.0^\circ$  in water. l- $\gamma$ -Benzoylaminovaleric acid, containing some of the racemic form, has  $[\alpha]_D^{20} 16.5^\circ$  in alcohol, and yields an impure l-aminovaleric acid, having  $[\alpha]_D^{20} - 10.7^\circ$  in water.  
C. S.

**Preparation of the Free Esters of Amino-acids.** NICOLAI ZELINSKY, A. ANNENKOFF, and J. KULIKOFF (*Zeitsch. physiol. Chem.*, 1911, 73, 459—470).—The free amino-acid esters may be obtained from their hydrochlorides by heating with excess of lead hydroxide. The procedure is as follows: the hydrochlorides of the esters are prepared as usual by the action of hydrogen chloride on a solution of the amino-acid in absolute alcohol, the alcohol is evaporated in a vacuum, the residue mixed with lead hydroxide, and the mixture distilled in a vacuum, when almost pure ester is obtained with a yield of 85—95% of the possible.

Ethyl  $\alpha$ -aminoisobutyrate has b. p.  $38.5-41^\circ/10$  mm.,  $D_D^{20} 1.0974$ ,  $n_D^{20} 1.4169$ .

Ethyl alanine has b. p.  $49-51^\circ/10$  mm.; ethyl  $\alpha$ -iminopropionate obtained at the same time showed b. p.  $114-115^\circ/10$  mm.,  $D_D^{20} 1.0152$ ,  $n_D^{20} 1.4728$ .

Ethyl 1-aminocyclopentane-1-carboxylate has b. p.  $80^\circ/10$  mm.,  $D_D^{20} 1.0292$ ,  $n_D^{20} 1.4531$ . Ethyl 1-aminocyclohexane-1-carboxylate has b. p.  $100^\circ/14$  mm.,  $D_D^{20} 1.0182$ ,  $n_D^{20} 1.4614$ . Both these esters are stable, and do not tend to form a diketopiperazine.

Ethyl methylaspartate is likewise very stable; it has b. p.  $112.5-113^\circ/12$  mm.,  $D_D^{20} 1.0632$ ,  $n_D^{20} 1.4332$ . Ethyl  $\alpha$ -methylamino-propionate has b. p.  $75-76^\circ/65$  mm.,  $D_D^{20} 1.4128$ ,  $n_D^{20} 1.4218$ , and can be kept for months in sealed tubes without change.  
E. F. A.

**Oxidation of the Amino-acids. II. Alanine and Tyrosine.** W. DENIS (*J. Biol. Chem.*, 1911, 10, 73—76. Compare this vol., i, 616).—The products of oxidation of alanine with alkaline potassium

permanganate are ammonia, carbon dioxide, oxalic, acetic and nitric acids. Tyrosine oxidised in the same way yields ammonia, carbon dioxide, oxalic, acetic and nitric acids, with traces of an acid which is probably *p*-hydroxybenzoic.

W. D. H.

**Conversion of Glycine into Iminodiacetic and Triglycolamic Acids.** MAX SIEGFRIED (*Zeitsch. physiol. Chem.*, 1911, 78, 194—203, Compare this vol., i, 427).—Much of the work described has been already abstracted (*loc. cit.*).

When glycine and mercuric chloride are set aside at 37° for several days, triglycolamic acid,  $N(CH_2 \cdot CO_2H)_3$ , m. p. 256—257° (decomp.), is obtained.

Alanine is not altered on similar treatment with mercuric chloride.

E. F. A.

**Poulenc's Sodium Glycerophosphate and a Free Glycerophosphoric Acid.** VINCENZO PAOLINI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 807—812).—The sodium glycerophosphate of Poulenc is prepared by a patented process by heating monosodium phosphate and glycerol. It has the composition of a *disodium glycerophosphate*,  $Na_2(C_3H_5O_2)PO_4$ . This indication that it is a chemical individual is confirmed by the fact that the author has prepared pure brucine  $\beta$ -glycerophosphate (Tutin and Hann, *Trans.*, 1906, 89, 1749) in good yield from the free acid obtained from it by way of the *silver* salt.

R. V. S.

**The Configuration of the Benzene Nucleus.** WILHELM VAUBEL (*Zeitsch. angew. Chem.*, 1911, 24, 1759—1760).—Polemical against Lifschitz (this vol., i, 622).

T. S. P.

**Old and New Benzene Formulæ.** ISRAEL LIFSCHITZ (*Zeitsch. angew. Chem.*, 1911, 24, 1760).—A reply to Vaubel (compare preceding abstract).

T. S. P.

**Polymerisation of Diethylene Hydrocarbons. II. Polymerisation and Isomerisation of *as*-Dimethylallene.** SERGIUS V. LEBEDEV (J. Russ. Phys. Chem. Soc., 1911, 43, 820—835. Compare this vol., i, 26).—When *as*-dimethylallene is heated in sealed tubes at 100—225° for two to twenty days, according to the temperature, it yields dipentene, the two following dimerides, and also a trimeride, the investigation of which is now proceeding. It will be seen that these products are both derivatives of cyclobutane.

1:2-Diisopropenylcyclobutane,  $\begin{array}{c} CH_2 \cdot C \cdot CMe_2 \\ | \quad | \\ CH_2 \cdot C \cdot CMe_2 \end{array}$  is a colourless liquid with a faint, aromatic smell, b. p. 61—62°/9 mm., 179—181°/753 mm.,  $D_4^{20}$  0.8571,  $D_4^{25}$  0.8422,  $n_D^{27}$  1.50086,  $n_D^{37}$  1.52345. It has the normal molecular weight in freezing benzene, and readily oxidises in the air. With nitrous acid, it gives a crystalline substance, m. p. 141°. When hydrogenated in presence of platinum black it yields

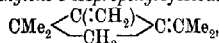
1:2-Diisopropenylcyclobutane,  $\begin{array}{c} CH_2 \cdot CH \cdot CMe_2 \\ | \quad | \\ CH_2 \cdot CH \cdot CMe_2 \end{array}$ , which is a faint smell-

ing liquid, b. p. 157°—158.5°/760 mm.,  $D_4^{20}$  0.7901,  $D_4^{25}$  0.7755,  $n_D^{20}$  1.42787,  $n_D^{25}$  1.42755. This compound is also formed, together with a decane, b. p. 153°—155.5° (impure), when the hydrogenation is carried out in presence of reduced nickel at 275° and a pressure of 100 atmospheres.

The action of ozone on 1:2-diisopropenylcyclobutane yields an ozonide which, when decomposed with water, gives 1-isopropenyl-2-cyclobutanone,  $\text{CH}_2 \begin{smallmatrix} \text{CO} \\ \text{CH}_2 \end{smallmatrix} \text{C}:\text{CMe}_2$ , as a slightly yellow liquid with a strong odour, recalling that of *p*-benzoquinone, b. p. 57°/11 mm., 171°/760 mm.,  $D_4^{20}$  0.9326,  $n_D^{20}$  1.48618,  $n_D^{25}$  1.50571; it absorbs oxygen from the air. It forms a phenylhydrazone, yellow needles, and a semicarbazone,  $\text{C}_{18}\text{H}_{18}\text{ON}_3$ , m. p. 241°. Attempts to convert the ketone into the corresponding 1:2-dione resulted only in the formation of succinic anhydride and condensation products. Oxidation with nitric acid (1:1) gave a theoretical yield of succinic acid. In the preparation of the ozonide, the latter is accompanied by succinic anhydride, acetone peroxide, and acetone, these being evidently formed by the decomposition of an unstable diozonide.

1-isoPropyl-2-cyclobutanone,  $\text{CH}_2 \begin{smallmatrix} \text{CO} \\ \text{CH}_2 \end{smallmatrix} \text{CHPr}^s$ , obtained by the action of hydrogen on the unsaturated ketone in presence of platinum black, has b. p. 148°—150°/770 mm.,  $D_4^{20}$  0.8704,  $n_D^{20}$  1.42827,  $n_D^{25}$  1.43843. The semicarbazone,  $\text{C}_8\text{H}_{15}\text{ON}_3$ , m. p. 183°, was prepared.

1:1-Dimethyl-2-methylene-3-isopropenylcyclobutane,



is a colourless liquid with an odour resembling that of kerosene, b. p. 37°—39°/9 mm., 149°—150°/752 mm.,  $D_4^{20}$  0.8143,  $D_4^{25}$  0.7982,  $n_D^{20}$  1.46769,  $n_D^{25}$  1.48623. With nitrous acid it gives a crystalline product, m. p. 100° (decomp.).

1:1:2-Trimethyl-3-isopropenylcyclobutane,  $\text{CMe}_2 \begin{smallmatrix} \text{CHMe} \\ \text{CH}_2 \end{smallmatrix} \text{CHPr}^s$ ,

obtained by hydrogenating the preceding compound under a pressure of 35 atmospheres in presence of platinum black, is a liquid, b. p. 145°—146.5°/760 mm.,  $D_4^{20}$  0.7744,  $D_4^{25}$  0.7598,  $n_D^{20}$  1.41997,  $n_D^{25}$  1.42980.

The action of ozone on 1:1-dimethyl-2-methylene-3-isopropenylcyclobutane yields various condensed products, *as*-dimethylsuccinic acid and an ozonide, which, as would be expected from the unsymmetrical character of the original hydrocarbon and the consequent formation of two mono-ozonides, gives the following two ketones (together with formic acid, acetone, and acetone peroxide) when decomposed with water.

1:1-Dimethyl-2-methylene-3-cyclobutanone,  $\text{CMe}_2 \begin{smallmatrix} \text{C}(\text{CH}_2) \\ \text{CH}_2 \end{smallmatrix} \text{CO}$ , is a

faintly yellow liquid with a pungent odour, b. p. 59°—60°/50 mm.,  $D_4^{20}$  0.8854,  $D_4^{25}$  0.8684,  $n_D^{20}$  1.44654,  $n_D^{25}$  1.46123. It readily oxidises in the air, depositing crystals, m. p. 129°, which emit a flash of light when heated. Its semicarbazone,  $\text{C}_8\text{H}_{13}\text{ON}_3$ , has m. p. 160°—190° (decomp.).

1 : 1-Dimethyl-3-isopropenyl-2-cyclobutanone,  $\text{OMe}_2\text{C}(\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2)\text{C}(\text{CH}_3)_2$ , b. p. 58–65°/11.5 mm., is very unstable, and was not obtained pure. T. H. P.

Hydrogenation in the Presence of Finely Divided Palladium. II. PIERRE BRETEAU (*Bull. Soc. chim.*, 1911, [iv], 9, 764–770. Compare this vol., i, 123).—Phenanthrene can be reduced electrolytically, using spongy palladium deposited on a platinum-iridium gauze cylinder as a cathode. The hydrogenation takes place in an alcoholic sulphuric acid solution with a current of 10 amperes and 8 volts. The tetrahydrophenanthrene after precipitation by water is extracted with ether. W. G.

Nitration of *o*-, *m*-, and *p*-Nitrobenzoyl-*p*-anisidines. FRÉDÉRIC REVERDIN (*Compt. rend.*, 1911, 153, 278–279; *Arch. sci. phys. nat.* 1911, [iv], 32, 124–134\*).—The nitro-group in the three nitrobenzoyl-*p*-anisidines is without influence on the course of nitration when these substances are treated with nitric acid, alone or in acetic acid solution. In each case, according to the conditions, orange mononitro-derivatives, yellow dinitro-derivatives, or colourless trinitro-compounds are formed. On hydrolysis, these substances give 3-nitro-, 2 : 3-dinitro-, and 2 : 3 : 6-trinitro-*p*-anisidine respectively, thus proving their constitution. The *o*-nitrobenzoyl derivatives and the trinitro-compounds are hydrolysed with ease by sulphuric acid, the others with difficulty. W. O. W.

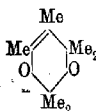
Crystallographic Study of Ethyl *iso*Succino-*p*-toluidate. ARISTIDE ROSATI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 921–922).—Ethyl *isosuccino-p*-toluidate,  $\text{C}_{12}\text{H}_{15}\text{O}_5\text{N}$  (compare Comanducci and Lobello, *Abstr.*, 1905, i, 271), forms large, colourless, tabular crystals, which belong to the monoclinic system [ $a : b : c = 3.4327 : 1 : 1.4716$ ;  $\beta = 68^\circ 49'$ ]. R. V. S.

Tetra- and Penta-methyl Orcinol. JOSEF HERZIG and FRANZ WENZEL [with KARL ZEIDLER] (*Monatsh.*, 1911, 31, 461–489).—Tetramethylorcinol, obtained on methylating orcinol in the nucleus, has been characterised by means of a dibromo-derivative, which is decomposed by dilute alkali hydroxide into fumaric acid and diisopropyl ketone.

In addition, a pentamethylorcinol is formed during methylation and characterised by a monobromo-derivative; it probably has the annexed formula. Tetramethylorcinol cannot be further methylated by methyl iodide and potassium hydroxide, and it is not therefore an intermediate product in the formation of pentamethylorcinol.

The yield of tetra- and penta-methylorcinol is unsatisfactory when working in methyl- or ethyl-alcoholic alkali hydroxide solution, and it appears to be more satisfactory in aqueous solution, where, however, pentamethylorcinol preponderates (compare Herzig and Erthal, following abstract).

\* and *Ber.*, 1911, 44, 2362–2369.



*Pentamethylorcinol* has m. p.  $8^{\circ}$ , b. p.  $120^{\circ}/12$  mm.

*Dibromotetramethylorcinol* separates in measurable monoclinic crystals, m. p.  $79.6^{\circ}$  [ $a:b:c=0.7243:1:0.9614$ ;  $\beta=98^{\circ}18'$ ]. It is readily decomposed on heating with very dilute potassium hydroxide into diisopropyl ketone, fumaric acid, and a saturated monobasic acid,  $C_{11}H_{16}O_4$ , m. p.  $165^{\circ}$ . With diazomethane a methyl ester is formed, m. p.  $64-67^{\circ}$ , which yields the original substance on hydrolysis. The acid is not decomposed by concentrated potassium hydroxide, and 30% hydrogen peroxide solution is without action. The acid is therefore regarded as a substituted cyclic complex.

[With A. SCHWADRON.]—*Monobromopentamethylorcinol*, after purification by distillation in a vacuum, was obtained in transparent, monoclinic plates [ $a:b:c=1.4653:1:0.7528$ ;  $\beta=91^{\circ}3'$ ], m. p.  $43-45^{\circ}$ . It is decomposed by dilute alkali hydroxide, yielding chiefly a neutral oil,  $C_{12}H_{18}O_3$ , insoluble in alkali hydroxide, b. p.  $117^{\circ}/16$  mm.,  $225-229^{\circ}/760$  mm. It is attempted to explain these decompositions by regarding the bromo-compounds as derivatives of norcarane, in which the cyclopropane ring undergoes rupture.

E. F. A.

**Alkylation in the Nucleus.** JOSEF HERZIG and BR. ERTHEL (*Monatsh.*, 1911, 32, 491—504. Compare Abstr., 1910, i, 667).—Tetramethylphloroglucinol when treated with methyl iodide and aqueous potassium hydroxide yields a mixture of hexa- and penta-methylphloroglucinol. Tetraethylphloroglucinol, however, when treated in the same way gives the methyl ether of tetraethylphloroglucinol, m. p.  $69-71^{\circ}$ , which is characterised by its resistance to alkaline hydrolysis. Phloroglucinol dimethyl ether under similar conditions chiefly yielded the trimethyl ether.

On methylation of orcinol in aqueous alkali, a mixture of tetra- and penta-methyl orcinol is obtained, but the tetramethyl derivative is not converted into the pentamethyl derivative in this manner.

With resorcinol the main product is a methyl ether of trimethyl-resorcinol, b. p.  $102-106^{\circ}/12$  mm. Quinol yields the dimethyl ether.

From phloroglucinol, aqueous potassium hydroxide, and ethyl iodide, the ethyl ether of *pentuethylphloroglucinol*, an oil, b. p.  $178-181^{\circ}/15$  mm., is obtained.

Silver phloroglucinolcarboxylate and ethyl iodide interact to yield almost entirely ethyl phloroglucinolcarboxylate, m. p.  $123^{\circ}$ . The amount of secondary action is very small; no product alkylated in the nucleus could be obtained, and the ester could be purified without difficulty. With methyl iodide secondary action takes place, and a product methylated in the ring is obtained.

Phloroglucinol and orcinol when methylated with methyl sulphate form a preponderating quantity of oxygen ethers, and homologues methylated in the nucleus could not be obtained.

Ethyl phloroglucinoldicarboxylate is quantitatively and without difficulty converted by diazomethane into the trimethyl ether, m. p.  $88-91^{\circ}$ .

Diazomethane is without action on ethyl succinylsuccinate.

E. F. A

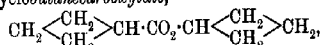


**Hexa- and Penta-methylphloroglucinol.** JOSEF HERZIG and BA. ERTHAL (*Monatsh.*, 1911, 32, 505—508. Compare Abstr., 1910, i, 607).—Hexamethylphloroglucinol does not react with *p*-nitrophenylhydrazine, semicarbazide, or amyl nitrite; it could not be reduced. It reacts with magnesium methyl iodide, forming a compound,  $C_{15}H_{20}O_6$ , m. p. 258—260°, which does not contain a methoxyl group, and is resistant towards the usual reagents.

Magnesium methyl iodide reacts with the methyl ether of penta-methylphloroglucinol, forming a substance,  $C_{15}H_{22}O_5$ , m. p. 67—68°, which likewise contains no methoxyl group. E. F. A.

**Two Methods of Obtaining cycloButanol. Certain Transformations of cycloButanol Accompanied by Isomerisation.** NICOLAUS J. DEMJANOFF and M. N. DOJARENKO (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 835—846).—It has been shown by Demjanoff (Abstr., 1908, i, 85) and by Zelinsky and Gutt (Abstr., 1908, i, 14) that the cyclobutanol obtained by Perkin (Trans., 1894, 65, 950) by the action of nitrous acid on cyclobutylamine contains an admixture of cyclopropylcarbinol. The alcohol obtained by Dalle (Abstr., 1902, i, 525) by the action of nitrous acid on cyclopropylmethylamine is also a mixture of cyclopropylcarbinol and cyclobutanol. In order to prepare pure cyclobutanol, the authors have, therefore, had recourse to Simonini's method (Abstr., 1893, i, 391), and to the electrolysis of a solution of potassium cyclobutanecarboxylate containing potassium carbonate and potassium hydrogen carbonate (compare Hofer and Moest, Abstr., 1902, i, 736). The principal result of the experiments described below is that the ring of cyclobutanol is unstable towards acid reagents, and gives rise to compounds containing a cyclopropane ring.

cycloButyl cyclobutanecarboxylate,



obtained in a 34.5% yield by the interaction of dry iodine and silver cyclobutanecarboxylate ( $2C_4H_7 \cdot CO_2Ag + I_2 = C_4H_7 \cdot CO_2 \cdot C_4H_7 + CO_2 + 2AgI$ ), is a liquid, b. p. 198.5—199°/750 mm.,  $D_{20}^{25}$  1.003,  $D_{20}^{25}$  1.007,  $D_{20}^{25}$  0.9980,  $n_D^{18.5}$  1.4551. Hydrolysis of this ester yields cyclobutanecarboxylic acid and cyclobutanol, b. p. 123°/735 mm.,  $D_{15}^{15}$  0.9226,  $D_{15.9}^{15.9}$  0.9206,  $D_{20}^{25}$  0.9181,  $n_D^{18.9}$  1.4339. On oxidation with nitric acid, it yields succinic acid, which is formed only in comparatively small quantity from cyclopropylcarbinol under similar conditions.

cycloButanol and cyclobutyl cyclobutanecarboxylate are also obtained as the products of hydrolysis of potassium cyclobutanecarboxylate.

Oxidation of cyclobutanol with chromic oxide and sulphuric acid gives, not cyclobutanone, but the isomeric cyclopropanaldehyde (compare Abstr., 1908, i, 156).

In spite of small differences in the b. p. and sp. gr., the acid obtained by converting cyclobutanol into the bromo-derivative and treating the magnesium compound of the latter with carbon dioxide (*ibid.*) bears a decided resemblance to allylacetic acid. T. H. P.

***p*-Hydroxybenzyl-methylamine and -dimethylamine.** MAR TIFFENEAU (*Bull. Soc. chim.*, 1911, [iv], 9, 825—828).—*p*-Hydroxy

*benzylmethylamine*,  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NHMe}$ , is obtained as the *hydriodide*, m. p. 149—150° (approx.), by the action of hydriodic acid on *p*-methoxybenzylmethylamine,  $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NHMe}$ ,  $D_4^0$  1.025, b. p. 121°/14 mm. (*hydrochloride*, m. p. 166°), itself formed by the interaction of anisyl chloride,  $D_4^0$  1.072, b. p. 116—120°/15 mm., or bromide,  $D_4^0$  1.395, b. p. 129°/6 mm. (approx.), and methylamine in alcohol in a closed tube. Some *di-p*-methoxybenzylmethylamine,  $D_4^0$  1.0794, b. p. 210°/15 mm., is also formed in this reaction. On demethylation, it gives *di-p*-hydroxybenzylmethylamine,  $\text{NMe}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH})_2$ , the *hydrochloride* of which has m. p. 197—199°.

*p*-Hydroxybenzyltrimethylamine,  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NMe}_3$ , m. p. 112°, reduces ammoniacal silver nitrate, Millon's reagent, or iodic acid, but does not give any coloration with ferric chloride; the *hydrochloride*, m. p. 194°, and the *hydriodide*, m. p. 135°, are both crystalline. It is produced in a manner analogous to its lower homologue by demethylating *p*-methoxybenzyltrimethylamine,  $D_4^0$  0.9878,  $D_{15}^0$  0.976, b. p. 110—111°/16 mm., which furnishes a *hydrochloride*, m. p. 157°, *hydriodide*, m. p. 145°, and *methiodide*, m. p. 158°. The last-mentioned substance on demethylation by hydriodic acid furnishes *p*-hydroxybenzyltrimethylammonium iodide,  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NMe}_3\text{I}$ , m. p. 191°, which is readily transformed by silver chloride into the corresponding *chloride*, m. p. 98°.

*p*-Methoxybenzyltrimethylamino is converted by acetic anhydride into anisyl alcohol and dimethylacetamide, and the demethylated base is similarly transformed by this reagent.

T. A. H.

3:4:5-Trinitroveratrole. ALFONS KLEMENC (*Monatsh.*, 1911, 32, 457—459).—3:4:5-Trinitroveratrole, m. p. 144—145°, has been described by Tiemann and Matsumoto (this Journ., 1876, ii, 524) and by Blanksma (*Abstr.*, 1905, i, 277).

It is now obtained on nitrating hemipinic acid with fuming nitric acid without a solvent and also by heating 5:6-dinitro-2:3-dimethoxybenzoic acid with fuming nitric acid, a method of preparation which establishes its constitution.

E. F. A.

Dehydration of the Glycols of Anethole and *iso*Safrole. VINCENZO PAOLINI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 940—946).—The author dissociates himself from the attack (*Abstr.*, 1908, i, 901) of his former collaborator Balbiano (compare Balbiano and Paolini, *Abstr.*, 1906, i, 186) on the statements of Tiffeneau and Daufresne (*Abstr.*, 1907, i, 701), and confirms the statements of these authors.

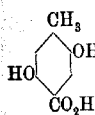
R. V. S.

Action of Bromine in Presence of Aluminium Bromide on *cyclo*Hexanol and *cyclo*Hexanone. FERNAND BODROUX and FELIX TABOURY (*Compt. rend.*, 1911, 153, 349—350).—Hexabromobenzene is formed when *cyclo*hexanol is dropped into excess of bromine containing 1% of aluminium in solution. *cyclo*Hexanone on treatment in the same way forms a *tetrabromo*-derivative crystallising in prisms, m. p. 117° (decomp.). When this is heated at 120—125°, it loses bromine

and hydrogen bromide, and becomes converted into a liquid having the properties of a bromophenol. Small quantities of uninvestigated substances of high melting point are also formed in this bromination.

W. O. W.

**Position of the Substituents in Hydroxyhomosalicylic [Dihydroxytoluic] Acid.** HANS SCHMID (*Monatsh.*, 1911, 32, 435—445).—*Toluquinol monoacetate* crystallises in long, lustrous

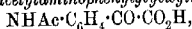


needles, m. p. 92°. The *diacetate* forms granular crystals, m. p. 49°; on oxidation in neutral solution with potassium permanganate, gentisic acid is obtained.

Dihydroxytoluic acid, prepared by heating toluquinol with potassium hydrogen carbonate and glycerol, forms a *diacetate*, m. p. 129°. This on oxidation with permanganate is converted into 2:5-dihydroxyterephthalic acid. Accordingly, dihydroxytoluic acid (hydroxyhomosalicylic acid) is represented by the annexed formula.

E. F. A.

*p*-Hydroxyphenylglyoxylic, *p*-Hydroxyphenylacetic, and *m*-Hydroxyphenylglycollic [*p*-Hydroxymandelic] Acids. JULIUS ALOY and CH. RABAUT (*Bull. Soc. chim.*, 1911, [iv], 9, 762—764).—By the oxidation of *p*-acetylaminooacetophenone by alkaline permanganate there results *p*-acetylaminophenylglyoxylic acid,



pale yellow crystals, m. p. 186—187°, which yields a white, crystalline silver salt, and a yellow *phenylhydrazone*, m. p. 200—202° (decomp.). This acid on hydrolysis and subsequent diazotisation yields *p*-hydroxyphenylglyoxylic acid (*Abstr.*, 1899, i, 288, 437). From the latter acid by reduction with hydriodic acid, *p*-hydroxyphenylacetic acid is formed.

*p*-Hydroxymandelic acid can be obtained from the corresponding glyoxylic acid by the action of sodium amalgam (compare Ellinger and Kotake, *Abstr.*, 1910, i, 384).

W. G.

**Theoretical Considerations on the Isomerism in Ethylene Derivatives.** EMIL ERLÉNMEYER (*Biochem. Zeitsch.*, 1911, 35, 149—165).—Substances of the general formula  $\text{C}(\text{R}^1\text{R}^2\text{R}^3) \cdot \text{C}(\text{R}^4\text{R}^5\text{R}^6)$  have been obtained in four modifications. If, however, the model representing these modifications, which are due to relative difference of position of the groups attached to each carbon atom, be twisted about the axis, then, according to van't Hoff, twelve modifications should exist. The author gives reasons for assuming that such do not really exist, although they have not been definitely isolated. These are (1) the results obtained in the determination of the crystallography and optical properties of the storax-cinnamic acids; (2) the fact that equimolecular quantities of phenyl-lactic acid and cinnamic acid are obtained by the reduction of phenylbromolactic acid and other similar reactions; (3) the existence of different malic acids, as demonstrated by Mayer and Aberson; (4) the fact that, according to Walde *l*-chlorosuccinic acid yields on treatment with potassium hydroxide t

*d*-malic acid, whereas by treatment with silver hydroxide the *l*-variety is obtained. If, in the case of ethylene compounds, the double bond between two multivalent elements be represented in the model in a similar manner to the bond between two groups, so as to form an angle, then, by the application of the above-mentioned conceptions as to the rotation of the model in the case of compounds of the  $C(R^1R^2R^3)-C(R^4R^5R^6)$  type, a whole series of isomeric derivatives with the ethylene linking should exist. This theory of the author is illustrated by his results with cinnamic acid, and numerous diagrams of the models are given in the paper.

S. B. S.

**The Possibility of the Existence of Molecular Asymmetric Storax-Cinnamic Acids.** EMIL ERLKENMEYER and G. HILGENDORFF (*Biochem. Zeitsch.*, 1911, 35, 134-148).—Storax-cinnamic acid was converted into the dibromo-derivative, and this substance, by distillation with steam, into *dl*-phenylbromolactic acid. The latter was separated into its antipodes by means of the cinchonine salts. The *d*- and *l*-bromo-acids were then converted by means of sodium amalgam into the corresponding *d*- and *l*-phenyl- $\beta$ -lactic acids, which, on treatment with hydrochloric acid at 46°, lose water and are converted into cinnamic acid. In only one case were the cinnamic acids thus obtained from optically active lactic acids themselves directly optically active. As, however, it is probable that optically active cinnamic acids, if they exist, have only a small rotation, it was possible that the amounts of such acids were too small in these preparations to affect the activity. They were therefore converted into the dibromides, and these substances into the sodium salts of the corresponding oxidoacrylates, as the authors have shown that the substances, if optically active, have a large rotation. It was found that the oxidoacrylates prepared from cinnamic acids which were obtained from optically active phenyl-lactic acids were active, the rotation corresponding in direction with that of the lactic acid from which they were obtained. Furthermore, a few of the crystals of the cinnamic acids obtained from optically active lactic acids showed asymmetric structure, whereas the crystals of storax-cinnamic acid itself were symmetrical.

Attempts were also made to prepare active cinnamic acids by the direct reduction of the active phenylbromolactic acids by means of zinc and alcohol, and it was found that this reaction yielded equal molecules of cinnamic acids and phenyl- $\beta$ -lactic acids. The changes in the rotation during the reaction were also followed, and it was found that at the end of the reduction very little, if any, changes in the rotation had taken place. As the solution had a considerably higher rotation than could be accounted for by the phenyl-lactic acids they contained, the conclusion was drawn that the zinc salts of the cinnamic acids in the solution were active. On attempting to prepare the free acids from the zinc salts, the authors did not succeed in obtaining optically active acids, although they have obtained preparations from the optically active lactic acids showing distinct traces of asymmetry. They conclude that optically active cinnamic acids exist which are very readily racemised.

S. B. S.

**The Isomeric Acids of the Cinnamic Acid Series.** EMIL ERLKENMEYER (*Biochem. Zeitsch.*, 1911, 34, 355—386).—The differences between the natural storax-cinnamic acid and the synthetic acid obtained from benzaldehyde from various sources are summarised, and the crystalline measurements of the dibromides and dichlorides are given. It is concluded that the synthetic acid is a mixture of the storax acid with heterocinnamic acid; the properties of these latter acids are contrasted, and the crystalline measurements of the dibromides are given. The separation of the two acids present in the synthetic acid can be accomplished (1) by the fractional distillation of the ester; (2) by the incomplete addition of hypochlorous acid, the residue of unacted on acid consisting of the hetero- $\beta$ -acid; (3) by the fractional precipitation of the acid from a solution of the sodium salt. The evidence is then summarised, which tends to show that the various cinnamic acids are isomerides with the same chemical constitution. (a) The evidence is summarised tending to show that the differences are not due to accidental impurities. (b) The acids can be converted into dibromides, from which, by various reactions, the original acids can be regenerated in unchanged form. Eight such series of reactions are mentioned. (c) It is shown that benzaldehydes of different origin yield different cinnamic acids, those aldehydes containing hydrocyanic acid yielding storax-cinnamic acid, whereas the aldehydes which have been completely separated from hydrocyanic acid yield the synthetic (mixed acids) cinnamic acid. The differences depend therefore on the grouping contained in the benzaldehyde. (d) Evidence is summarised to show that the differences are not due to impurities in the aldehyde. (e) Finally, evidence is brought forward to show that in the process, by removal of the hydrocyanic acid from the natural aldehydes in which calcium hydroxide is used, the aldehyde undergoes isomeric change, due to the presence of alkali. Furthermore, if storax-cinnamic acid be oxidised to benzaldehyde, care being taken to prevent the mixture from becoming alkaline, an aldehyde is obtained from which, by Perkin's synthesis, the original acid can be regenerated. If, however, the oxidation of the acid to benzaldehyde be carried out in alkaline solution, an aldehyde is obtained from which, by the Perkin synthesis, instead of storax-cinnamic acid, a mixture of this and the hetero- $\beta$ -acid (synthetic cinnamic acid) is obtained. S. B. S.

**The Behaviour of Certain Mixtures of Storax Cinnamic Acid with Certain Substituted Cinnamic Acids.** EMIL ERLKENMEYER and G. HILGENDORFF (*Biochem. Zeitsch.*, 1911, 34, 405—416).—To ascertain definitely whether the synthetic acid differs from the storax acid, owing to the presence of certain impurities, the properties of the mixture of this acid with substituted cinnamic acids (chloro-, hydroxy-, methoxy-, and methyl derivatives) were investigated. Experiments on the separation of *p*-methylcinnamic acid from cinnamic acid were carried out. Crystallographic measurements of the mixtures were also made. The results confirm the statement in a previous paper, that the synthetic acid is not a mixture of cinnamic with a substituted cinnamic acid. S. B. S.

**Further Experiments on the Separation of Heterocinnamic Acid.** EMIL ERLENMEYER and G. HILGENDORFF (*Biochem. Zeitsch.*, 1911, 34, 417—427).—A series of experiments on the fractional precipitation of the synthetic cinnamic acid from the solution of the sodium salt by acid are described, which were undertaken with the object of determining whether the hetero-acid could be further separated into other constituents. As no acid other than the hetero-acid could be isolated by this method, the conclusion is drawn that this is the only acid accompanying the storax-cinnamic acid present in the synthetic product. S. B. S.

**Action of Anisaldehyde and Piperonaldehyde on the Sodium Derivative of Phenylacetoneitrile.** FERNAND BODREUX (*Compt. rend.*, 1911, 153, 350—351).—Anisaldehyde and piperonaldehyde react with the sodium derivative of phenylacetoneitrile, forming the unsaturated nitriles,  $\alpha$ -phenyl-*p*-methoxycinnamoneitrile (Frost, Abstr., 1889, 597) and  $\alpha$ -phenyl-3:4-methylenedioxcinnamoneitrile (Walther and Wetzlich, Abstr., 1900, i, 438) respectively. On hydrolysis these substances yield  $\alpha$ -phenyl-*p*-methoxycinnamic acid,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CPh}\cdot\text{CO}_2\text{H}$ , needles, m. p. 188°, and  $\alpha$ -phenyl-3:4-methylenedioxcinnamic acid,  $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{CPh}\cdot\text{CO}_2\text{H}$ , needles, m. p. 233°. W. O. W.

**Interchange of Primary, Secondary, and Tertiary Alkyl Groups in the Esters of Organic Acids.** MICHAEL PFANNL (*Monatsh.*, 1911, 32, 509—522. Compare Abstr., 1910, i, 480; also Kommenos, Abstr., 1910, i, 361).—The experiments were made to establish the interchange of secondary and tertiary alcohols with primary, and to show the influence of the nature and structure of the alkyl group on the reaction velocity. The esters of terephthalic acid were allowed to react with methyl alcohol in proportions, so that the equivalent of 0.5 gram of dimethyl terephthalate was present in 10 c.c. of methyl alcohol. Under these conditions about 20% of change is indicated by the crystallisation of the dimethyl ester.

Under similar conditions the diethyl ester required 1 min. 40 sec. for 20% conversion into dimethyl ester, the di-*n*-propyl ester required 3 min. 50 sec., the di-*n*-butyl ester 3 min. 30 sec., the diisobutyl ester 5 min. 40 sec., the diisopropyl ester 14 min. 10 sec., whilst the di-*tert*-butyl ester did not react within forty-eight hours. It is obvious that retardation is caused by the branching of the chain, particularly by the secondary and tertiary character of the alkyl.

Whereas methyl is interchanged with the *sec*-isopropyl group in the esters of terephthalic acid at the ordinary temperature and with very little alkali, the *tert*-butyl group can only be introduced by using much alkali and heating.

*tert*-Butyl benzoate, obtained in this manner from methyl benzoate and *tert*-butyl alcohol, is a highly refractive, oily liquid, very similar to other esters of benzoic acid; it has b. p. 94°/10 mm., 213°/760 mm., decomposing to benzoic acid when distilled.

Di-*n*-butyl terephthalate forms long, colourless needles, m. p. 16°.

*Di-tert.-butyl teraphthalate* crystallises in stout, lustrous prisms, m. p. 118°; it is obtained by fractional distillation of the product obtained by heating the dimethyl ester with *tert.*-butyl alcohol and excess of alkali hydroxide. E. F. A.

**Friedel-Crafts' Reaction.** OTTOKAR HALLA (*Monatsh.*, 1911, 32, 637—640).—On heating xanthone with the equivalent quantity of phthalic anhydride, dissolved in benzene containing a little toluene, and aluminium chloride, no interaction with the xanthone was found to take place, but the reaction mixture contained benzoylbenzoic and toluoylbenzoic acids.

Experiments made with varying proportions of toluene showed that when phthalic anhydride, in equivalent quantity to the toluene taken, was used in every case, toluoylbenzoic acid was the sole product.

It was supposed that benzoylbenzoic acid was first formed, and the benzoyl group subsequently displaced by toluoyl, as Heller and Schülke (*Abstr.*, 1908, i, 994) supposed in the case of naphthoylbenzoic acid. This displacement is proved, however, not to take place on heating benzoylbenzoic acid with toluene and aluminium chloride. The change is attributed to the ready substitution of the alkylated benzene nucleus. E. F. A.

**Glycocholic Acid and Para-glycocholic Acid.** EUGEN LETSCHE (*Zeitsch. physiol. Chem.*, 1911, 73, 308—311. Compare *Abstr.*, 1909, i, 587).—Glycocholic acid crystallises with  $1\frac{1}{2}H_2O$ ; it sinters at 126°, m. p. 130°. The anhydrous acid sinters at 130—132°, decomp. 154—155°. When heated at 100° in aqueous suspension for some hours, para-glycocholic acid is formed; it crystallises with  $1H_2O$ , sinters at 186°, decomp. 198°, or when anhydrous it sinters at 193°, decomp. 198°. The two acids are regarded as isomerides. E. F. A.

**Separation and Transformation of the Benzaldehydes.** EMIL ERLÉNMEYER, G. HILGENDORFF, and TH. MARX (*Biochem. Zeitsch.*, 1911, 34, 386—404).—The attempts made to separate the benzaldehydes from mixtures are described. Fractional distillation led to no satisfactory results. A partial separation could, however, be effected by fractional condensation with sodium acetate and acetic anhydride, or by fractional addition of hydrocyanic acid; owing to the fact that the isomerides possess different velocity fractions in these cases. Experiments are also described to show how the "natural" benzaldehyde can be converted into the "synthetic" benzaldehyde by the action of alkaline reagents, or by heating with platinised asbestos; attempts to convert the synthetic acid into the hetero- and stero-acids are also mentioned. S. E. S.

**The Electrolytic Reduction of Anisaldehyde.** JULIUS TAFEL and WILHELM SCHEFFS (*Ber.*, 1911, 44, 2148—2154).—In accordance with the results obtained by Tafel (*Abstr.*, 1909, i, 766) on the reduction of methyl *iso*-amyl ketone at cadmium cathodes, it was to be expected that the aldehyde group would undergo reduction to a greater extent at cathodes of this metal than at other cathodes. The authors

have, therefore, studied the electrolytic reduction of anisaldehyde in aqueous-alcoholic solution of sulphuric acid, investigating the influence of current density, temperature, and material of which the cathode was made, especially in so far as the yield of *p*-tolyl methyl ether,  $C_6H_4MeOMe$ , was concerned.

The complete reduction of the aldehyde group takes place to a much greater extent at cadmium electrodes than at electrodes of other metals. Under the conditions of current density and temperature given by Law (Trans., 1906, 89, 1512, 1520; 1907, 91, 748; 1911, 99, 1113), a 37% yield of *p*-tolyl methyl ether was obtained, and the yield could be further increased to 60% by increasing the current density, the temperature not being allowed to rise above 25°. The formation of anisic alcohol takes place to a slight extent only, whereas Law (*loc. cit.*) found the opposite to be the case with copper electrodes.

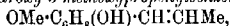
In addition to *p*-tolyl methyl ether and anisic alcohol, some resin is always formed, together with a mixture of solid substances of high boiling point, which contains the isomeric hydroanisols, dimethoxystilbene, and probably also dimethoxydibenzyl. The total quantity of these bimolecular products formed depends chiefly on the temperature, increasing very rapidly with rise in temperature. At 35°, however, the amount formed is independent of the strength of the current within fairly wide limits.

The formation of resin was always very small (0.5–7%), only becoming appreciable when very strong or too weak acid was used.

T. S. P.

**Phenolic Aldehydes. I. Reactivity of the Aldehyde Group in Phenolic Aldehydes.** HERMANN PAULY and RICHARD (FREIHER) VON BUTTLAR (*Annalen*, 1911, 383, 230–288).—Attention has been called by several investigators to the fact that certain aromatic aldehydes do not behave normally in the Grignard reaction. Béhal and Tiffeneau, in particular, obtain very poor yields of the expected propenyl compounds from protocatechualdehyde, *p*-hydroxybenzaldehyde, vanillin and isovanillin, and magnesium ethyl bromide, although the neutral ethers react normally (Abstr., 1908, i, 260).

[With KARL LOCKEMANN.]—It is now found that salicylaldehyde and magnesium ethyl iodide give, in 92% yield, a mixture of *o*-propenylphenol,  $OH \cdot C_6H_4 \cdot CH:CHMe$ , m. p. 34.8°, b. p. 229–231°, and a yellow oil, b. p. about 235°/23 mm., which is probably a bimolecular form of *o*-propenylphenol. So also, *o*-vanillin gives 46% of *o*-iso-eugenol (2-hydroxy-3-methoxypropenylbenzene),



m. p. 81° (bromo-*o*-iso-eugenol dibromide,  $C_{10}H_{11}O_2Br_2$ , m. p. 111°); 2:3-dimethoxybenzaldehyde yields 93% of 2:3-dimethoxyphenylmethylcarbinol,  $C_6H_3(OMe)_2 \cdot CHMe \cdot OH$ , b. p. 151–152°/15 mm.,  $D_4^{20}$  1.1213 (phenylurethane, m. p. 127°), and 2:3-dihydroxybenzaldehyde yields 83% of a substance, which is probably a polymericide,  $(C_6H_5O_2)_n$ , of *o*-propenylcatechol.

The striking difference of behaviour of the preceding aldehydes in the Grignard reaction has induced the authors to examine the reactivity of phenolic aldehydes in other directions. Their conclusions



that mono- and di-hydric phenolic aldehydes and their acyl derivatives show, in contrast to their neutral ethers, abnormal behaviour in the following reactions, are based to a large extent on observations already recorded in the literature, and are most concisely represented by the table (*a*=smooth reaction or yield greater than 75%; *b*=fair reaction or yield about 60%; *c*=bad reaction or yield about 30%; *d*=very bad or no reaction).

	Ethers of phenolic aldehydes.	Hydroxy-benz-aldehydes.			Dihydroxy-benz-aldehydes.			Vanilline.			cycloCarbonates of dihydroxybenz-aldehydes.		
		<i>o</i> .	<i>m</i> .	<i>p</i> .	2,3,2,4.	2,5.	3,4.	OH.	2.	3, 4.	OMe.	3.	4.
Cannizzaro reaction	<i>a</i>	<i>d</i>			<i>d</i>	<i>d</i>	<i>d</i>						
Benzoin condensation	<i>a</i>	<i>d</i>											
Acetal formation (by alcohol and HCl).	<i>b</i>	<i>d</i>	<i>d</i>					<i>d</i>	<i>d</i>	<i>d</i>			<i>d</i>
Acetal formation [by CH(OR) <sub>2</sub> ]	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>d</i>	<i>a</i>	<i>d</i>	<i>d</i>					<i>d</i>
Hydroxamic acid formation [by NH(OH) <sub>2</sub> ]	<i>a</i>	<i>c</i>	<i>a</i>	<i>d</i>				<i>d</i>		<i>a</i>	<i>d</i>		<i>d</i>
Grignard reaction	<i>a</i>	<i>a</i>	<i>c</i>	<i>a</i> (?)				<i>d</i>	<i>a</i> (?)	<i>c</i>	<i>c</i>		<i>d</i>
Doebner's reaction (CH <sub>3</sub> ·CO·CO <sub>2</sub> H and βC <sub>10</sub> H <sub>7</sub> ·NH <sub>2</sub> )	<i>a</i>	<i>a</i>	<i>a</i>	<i>b</i>	<i>d</i>	<i>d</i>	<i>d</i>	<i>b</i>	<i>a</i>	<i>a</i>	<i>b</i>		
Schiff's reaction (magenta and H <sub>2</sub> SO <sub>4</sub> )	<i>a</i>	<i>b</i>	<i>b</i>	<i>d</i>	<i>c</i>	<i>d</i>	<i>b</i>	<i>d</i>	<i>b</i>	<i>c</i>	<i>c</i>	<i>b</i>	<i>b</i>

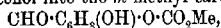
The diminution in the reactivity of the aldehyde group does not always coincide with the entrance of the first hydroxyl group, but usually is quite evident when the second hydroxyl group is introduced, particularly in the para-position with respect to the aldehyde group.

Various causes of the abnormalities are suggested and discussed. The original paper must be consulted for a comprehension of the only satisfactory explanation, which is based on Stark's electro-atomistic theory of valency.

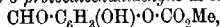
The following acetals have been obtained from methyl orthoformate by a modification of Claisen's process. *p*-Hydroxybenzaldehyde dimethyl acetal, OH·C<sub>6</sub>H<sub>4</sub>·CH(OMe)<sub>2</sub>, m. p. 60—64°, *m*-hydroxybenzaldehyde dimethyl acetal, b. p. 150°/11 mm. (decomp.); *o*-hydroxybenzaldehyde dimethyl acetal, b. p. about 65°/0.4 mm. These acetals are extremely sensitive to the action of alkalis, and the first and the last, when heated, lose methyl alcohol and yield substances which are apparently mixtures of the hydroxybenzaldehyde and the quinomethyl ether, O=C<sub>6</sub>H<sub>4</sub>·CH·OMe. The following mercaptals are described: *m*-Hydroxybenzaldehyde dimethyl mercaptal, OH·C<sub>6</sub>H<sub>4</sub>·CH(SMe)<sub>2</sub>, very viscous oil; *p*-hydroxybenzaldehyde dimethyl mercaptal, m. p. 73.5°; *protocatechu*aldehyde dimethyl mercaptal, m. p. 108—109°; *o*-protocatechu-aldehyde di-*p*-nitrobenzyl mercaptal, C<sub>6</sub>H<sub>3</sub>(OH)<sub>2</sub>·CH(S·CH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·NO<sub>2</sub>)<sub>2</sub>, m. p. 177°, yellow prisms; *gentisinaldehyde* di-*p*-nitrobenzyl mercaptal, m. p. 170°, green prisms. The following colours and m. p.'s refer to the substituted β-naphthacinehonic acids obtained by Doebner's method from the corresponding aldehydes: *m*-hydroxyphenyl-, yellow powder,

284.5°; *p*-hydroxyphenyl, pale yellow powder, 325.5°; *m*-hydroxy-*p*-methoxyphenyl, citron-yellow powder, 295°; *o*-hydroxy-*m*-methoxyphenyl, white powder, 251°; *mp*-dihydroxyphenyl- $\beta$ -naphthacinechonic acid, orange-yellow powder, 317.5°. C. S.

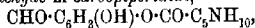
**Phenolic Aldehydes. II. Reactivity of the Phenolic Group in Phenolic Aldehydes.** HERMANN PAULY, KONRAD SCHÜBEL, and KARL LOCKEMANN (*Annalen*, 1911, 383, 288—337. Compare preceding abstract).—The acid character of a phenol is enormously increased by the entrance of an aldehyde group into the nucleus. By titration with phenolphthalein as indicator, 2:3-, 2:4-, and 2:5-dihydroxybenzaldehydes behave as monobasic acids, as do also protocatechualdehyde, vanillin, and *o*- and *p*-hydroxybenzaldehydes. The acidifying influence of the aldehyde group, therefore, is exerted on the hydroxyl group in any position in the nucleus, but it is least in the meta-position, and apparently is exerted only on one hydroxyl group, conductivity measurements showing that the  $k$  values of *p*-hydroxybenzaldehyde and protocatechualdehyde are  $2.2 \times 10^{-8}$  and  $2.8 \times 10^{-8}$  respectively at 25° (for phenol,  $k$   $1.3 \times 10^{-10}$  at 18°). Corresponding with the increased mobility (that is, the weakening of the union between the hydrogen and the oxygen atoms) of the hydrogen atom of the hydroxyl group in the para-position in protocatechualdehyde (as compared with the mobility of the hydrogen atom in phenol or catechol), experiment shows that a similar loosening is to be observed in the derivatives of the phenols; thus the *cyclocarbonate* of protocatechualdehyde, by treatment with water, evolves carbon dioxide about seventy-five times as rapidly as the *cyclocarbonate* of catechol. (This ratio is approximately the ratio of the  $k$  values of protocatechualdehyde and catechol [compare Rivett and Sidgwick, *Trans.*, 1910, 97, 1677]). Moreover, this loosening of the linking at the oxygen atom in the para-position (or in the ortho-position in the case of derivatives of 2:3-dihydroxybenzaldehyde) is seen in the following instances. Protocatechualdehyde *cyclocarbonate* is converted by boiling methyl alcohol into the *m*-methyl carbonate,



*m*. p. 96° (formerly given as 93°), the orientation of which is proved by methylation and subsequent hydrolysis, whereby *isovanillin* is obtained. Similarly, the *cyclocarbonate* of *o*-protocatechualdehyde is converted into *methyl o*-protocatechualdehyde-*m*-carbonate,



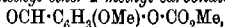
*m*. p. 115°, the orientation of the hydroxyl and aldehyde groups being shown by the exact analogy of the substance to salicylaldehyde. Again, protocatechualdehyde *cyclocarbonate* is converted by piperidine into *protocatechualdehyde-m-carbopiperidide*,



*m*. p. 123° (*phenylhydrazone*,  $\text{C}_{10}\text{H}_{21}\text{O}_3\text{N}_2$ , *m*. p. 159°), which yields *isovanillin* by methylation and subsequent hydrolysis. Finally, phenylhydrazine acts on the *cyclocarbonate* to form, first, the *phenylhydrazone*,  $\text{CO}_2\text{C}_6\text{H}_3\text{CH}:\text{N} \cdot \text{NHPh}$ , *m*. p. 177°, and then the *phenylhydrazoncarbophenylhydrazide*,  $\text{NHPh} \cdot \text{N}:\text{CH} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{O} \cdot \text{CO} \cdot \text{NH} \cdot \text{NHPh}$ , *m*. p. 186°.

The salts of phenolic aldehydes with the alkali metals and metals of the alkaline earths are frequently strongly coloured. The authors do not commit themselves by giving a quinonoid constitution to these salts; in fact, they are inclined against this view on account of the persistence of the colour in the presence of even fairly strong reducing agents.

*o*-Protocatechualdehyde (2:3-dihydroxybenzaldehyde) forms an *and*,  $C_6H_3(OH)_2 \cdot CH \cdot NPh$ , scarlet needles, m. p.  $135^\circ$ ;  $\beta$ -naphthylamine derivative,  $C_6H_3(OH)_2 \cdot CH \cdot N \cdot C_{10}H_7$ , bluish-red needles, m. p.  $164^\circ$ ; phenylhydrazone, m. p.  $167^\circ$  (not  $176^\circ$  as given previously); *semicarbazone*, m. p.  $226^\circ$  (corr., decomp.), and orange-yellow barium salt,  $C_6H_3O_3Ba \cdot 4H_2O$ , which loses  $2H_2O$  at  $105^\circ$  and another  $2H_2O$  at  $170$ – $180^\circ$ . The 3-methyl ether-2-methyl carbonate,

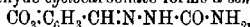


m. p.  $60^\circ$ , is obtained from the potassium salt of *o*-vanillin and methyl chlorocarbonate in benzene.

Protocatechualdehyde forms a yellow barium salt,  $C_7H_3O_3Ba \cdot 2H_2O$ , which loses one or two molecules of water at  $160$ – $170^\circ$  according to the duration of the heating, and an almost colourless barium hydrogen salt,  $(C_7H_3O_3)_2Ba \cdot 3H_2O$ . When the barium salt is heated with methyl sulphate (rather more than 1 mol.) in benzene, vanillin and isovanillin are obtained in equal amount, but when protocatechualdehyde is heated with alcoholic potassium hydroxide (rather more than 1 mol.) and methyl iodide, the ratio of isovanillin to vanillin is 9:1.

*Vanillin methyl 4-carbonate*,  $CHO \cdot C_6H_3(OMe) \cdot O \cdot CO_2Me$ , m. p.  $91.5^\circ$ , is obtained by heating vanillin and methyl-alcoholic potassium hydroxide with methyl chlorocarbonate. *isoVanillin methyl 3-carbonate*, m. p.  $121^\circ$ , is prepared by heating the sodium salt of isovanillin and methyl chlorocarbonate in benzene.

Protocatechualdehyde cyclocarbonate forms a *semicarbazone*,



m. p.  $220^\circ$  (decomp.), and reacts with methyl mercaptan in the presence of hydrogen chloride only at the aldehyde group (compare behaviour with methyl alcohol), forming the *dimethyl mercaptal*,  $CO_3 \cdot C_6H_3 \cdot CH(SMe)_2$ , m. p.  $56.5^\circ$ .

Salicylaldehyde and piperidine (2 mols.) react to form the *dipiperidyl*,  $OH \cdot C_6H_4 \cdot CH(NC_3H_7)_2$ , m. p.  $87$ – $88^\circ$ , colourless plates. Gentisin-aldehyde forms a *semicarbazone*,  $C_6H_3(OH)_2 \cdot CH \cdot N \cdot NH \cdot CO \cdot NH_2$ , m. p.  $249^\circ$ . An attempt to form an *aci*-ether of salicylaldehyde has not given a conclusive result.

C. S.

**Theory of the Phenomena of Halochromy. II.** PAUL PFEIFFER [and, in part, B. FRIEDMANN, Z. GOLDBERG, E. PROS, and V. SCHWÄRZKOPF] (*Annalen*, 1911, 383, 92–155. Compare Abstr., 1910, i, 852).—The author's theory of halochromy is based on the conception that the molecule of the metallic salt or acid (termed the addendum for brevity) unites as a whole co-ordinatively at the carbonyl oxygen atom, thereby neutralising its free affinity, and consequently increasing the free affinity of the carbonyl carbon atom, which thus becomes more unsaturated and acquires the character of a chromophore; the

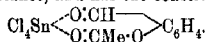
phenomenon of halochromy is ascribed to the presence of such unsaturated carbon atoms.

The halochromatic substances previously described (*loc. cit.*) containing tin tetrahalides as addenda, are almost invariably composed of 2 mols. of the carbonyl compound and 1 mol. of the tin tetrahalide, are represented by the constitution  $X_4Sn \begin{smallmatrix} \text{O:CRR'} \\ \text{O:CRR'} \end{smallmatrix}$ , and are colourless,

or nearly so, on account of the relatively simple constitution of the organic component. The substances now described contain aromatic carbonyl compounds, and are usually highly coloured; they are still composed of 2 mols. of the carbonyl compound and 1 mol. of the tin tetrahalide, and therefore receive the constitution given above. Since this constitution is general for halochromatic substances containing a tin tetrahalide, it probably holds for substances containing other addenda.

The colour, but not the composition, of halochromatic substances of the type  $X_4Sn \begin{smallmatrix} \text{O:CRR'} \\ \text{O:CRR'} \end{smallmatrix}$  (where R and R' are either or both aromatic) is influenced by the presence of chromophores in R and R'.

The influence of auxochromic groups in R and R' is interesting. The organic components are the isomeric hydroxybenzaldehydes, methoxybenzaldehydes, and the hydroxyacetophenones, the addendum being a tin tetrahalide, an acid, or an alkali. The presence of the auxochrome intensifies the colour of the halochromatic substance, its influence being greatest when it is ortho to the carbonyl group and least in the para-position; however, when an ethenoid group is present between the aromatic nucleus and the carbonyl group (for example, the isomeric hydroxy- or methoxy-cinnamic acids), the influence of the auxochrome on the colour of the halochromatic substance is normal, being greatest in the ortho- and least in the meta-position. When the hydroxyl group is acetylated, colour disappears; thus *acetylsalicylaldehyde tin tetrachloride* is an unstable, greyish-white, crystalline substance, and has the constitution



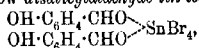
The dependence of halochromy on the functional nature of the carbonyl compound is illustrated by comparing the halochromy of a series of additive compounds obtained from carbonyl compounds  $R\cdot CO\cdot A$  (where A is a hydrogen atom or an alkyl, hydroxy-, alkyloxy-, or amino-group) and an addendum which is either (i) concentrated sulphuric acid, (ii) hydrogen chloride in alcohol or glacial acetic acid, (iii) aqueous potassium hydroxide, (iv) aqueous ammonia, or (v) tin tetrachloride. When  $R\cdot CO\cdot$  is a benzoyl, hydroxybenzoyl, or cinnamoyl group, pronounced halochromy is observed only when the addendum is (i) and A is a hydrogen atom or an alkyl group. The explanation of this behaviour is as follows. Evidently the degree of unsaturation of the carbonyl carbon atom (which is essentially the cause of halochromy) must be influenced by the nature of R and A. When these are able to neutralise a portion of the free affinity of the carbonyl carbon atom (as, for example, when A is OH, OR', NH<sub>2</sub>, NR', etc.), its chromophoric character is weakened, and the additive com-

pounds will be colourless or less coloured than those in which A is a hydrogen atom or an alkyl group. (In this connexion it is instructive to contrast the absence of selective absorption in oxalic acid, ethyl oxalate, and oxamide with the yellow colour of glyoxal and of dimethyl diketone.)

The influence of the addendum on halochromy can be ascertained by comparing a series of additive compounds,  $X \cdots O \cdot CRR'$ , containing different X's. The author's theory requires that the colour should be more intense the stronger the attachment of the addendum to the carbonyl oxygen atom. There is no doubt that such attachment is exceptionally strong when X is  $H_2SO_4$ , because almost without exception the colour produced by carbonyl compounds with (i) is more intense than with (ii) or (v) in the list of addenda given above. Unfortunately, there is no method of measuring the attachment of sulphuric acid to the carbonyl oxygen atom. However, according to the ionic theory, the greater the strength of an acid, the more easily is the acidic hydrogen ionised, and therefore the greater the amount of its free affinity. Consequently, carbonyl compounds should form more intensely coloured additive compounds with strong acids than with weak acids of similar constitution. This deduction, which can also be reached by a consideration of Werner's dissociation theory, has been proved by Stobbe and Haertel's experiments on salts of distyryl ketone, etc., and on the colours of solutions of a given ketone in acid having different dissociation constants (Abstr., 1910, i, 43).

When the negative constituent Y of an acid HY unites with a molecule B, forming  $HY \cdots B$ , a little consideration shows that the carbonyl carbon atom is more unsaturated in the additive compound  $RR'CO \cdots HY \cdots B$  than in  $RR'CO \cdots HY$ ; this explains why the hydrochlorides of carbonyl compounds are less coloured than the mercurichlorides and stannichlorides, and also why the acid salts of carbonyl compounds [which the author regards as being constituted like the mercurichlorides; for example,  $(CHPh:CH)_2CO \cdots HCl, HCl$ ] are more coloured than the normal salts.

The author's explanation of the catalytic action of acids or metallic salts (*loc. cit.*) would be greatly strengthened if the unsaturated character of the "binary" compound of the acid or metallic salt and the carbonyl compound could be directly proved by the formation of a "ternary" compound by the addition of a third molecule at the carbonyl carbon atom. Such addition would neutralise more or less the free affinity of the carbon atom, and such "ternary" compounds would be less coloured than the "binary" compounds; thus yellow *disubstituted aldehyde tin tetrabromide*,



is easily converted by exposure to the air into a colourless *dihydrate*,  $2C_6H_4(OH) \cdot CHO, SnBr_4, 2H_2O$ , and the orange-red additive compound of distyryl ketone and tin tetrachloride unites with benzene to form an orange-yellow substance,  $2(CHPh:CH)_2CO, SnCl_4, C_6H_6$ .

Meyer states that the additive compounds of metallic salts and quinones correspond completely with the similar compounds of ordinary ketones (Abstr., 1909, i, 395; 1910, i, 179). The author

considers, therefore, that the colour phenomena of quinhydrones, of merquinonoid compounds, and of the compounds of quinones and alkali phenoxides are explicable by his theory of halochromy. In these cases the unsaturated carbonyl carbon atoms are present in a ring, and their influence on selective absorption is materially strengthened by the presence of the ethenoid linkings.

Triphenylmethyl halides form with metallic salts intensely coloured additive compounds, which are generally regarded as  $CPh_3X \cdots M$ . The methane carbon atom, therefore, becomes unsaturated (triphenylmethyl may be regarded as an extreme case) and chromophoric, and this class of additive compounds falls into line with the author's theory; also, in the triphenylmethane dyes the colour may depend essentially on the presence of the central unsaturated carbon atom, the action of which is increased by auxochromic OH and  $NH_2$  groups.

Finally, by reasoning based on his researches on the molecular compounds of the tin series, the author arrives at conclusions regarding Walden's inversion which do not differ much from those recently expressed by Werner and by Fischer.

The preceding statements are illustrated by reference to compounds in the literature and to the following new substances, which are obtained, as a rule, by the direct interaction of the two components in a non-hydroxylic solvent, usually benzene, occasionally ether or chloroform. (When not given, the formula is normal.) *Disalicylaldehyde tin tetrachloride*, deep yellow crystals, m. p.  $152^\circ$ ; *disalicylaldehyde tin tetrabromide*, deep yellow crystals, m. p.  $100^\circ$ ; *salicylaldehyde hydrobromide*,  $OH \cdot C_6H_4 \cdot CHO \cdot HBr$ , unstable, yellow prisms; *di-o-methoxybenzaldehyde tin tetrachloride*, yellow, crystalline powder, m. p.  $180-181^\circ$ ; *di-o-methoxybenzaldehyde tin tetrabromide*, yellow, crystalline powder, m. p.  $131^\circ$ ; *di-m-hydroxybenzaldehyde tin tetrachloride* and the *tin tetrabromide* are yellow, crystalline substances; *di-m-methoxybenzaldehyde tin tetrachloride*, yellowish-grey powder; *dipiperonal tin tetrachloride*, yellow, crystalline powder, blackening at  $130-190^\circ$ ; *dipiperonal tin tetrabromide*, pale yellow, crystalline powder, m. p.  $150^\circ$ ; *di-p-dimethylaminobenzaldehyde tin tetrachloride* and also the *tin tetrabromide*, canary-yellow substances; *di-o-nitrobenzaldehyde tin tetrachloride*, colourless, prismatic needles, m. p.  $80-120^\circ$ ; *di-m-nitrobenzaldehyde tin tetrachloride*, colourless, crystalline; *di-p-nitrobenzaldehyde tin tetrachloride*, pale yellow, prismatic needles containing  $C_6H_6$ , half of which is easily lost, substance then has m. p.  $101^\circ$ ; *di-m-hydroxyacetophenone tin tetrachloride*, yellow, crystalline, m. p.  $99^\circ$ ; *di-p-hydroxyacetophenone tin tetrachloride*, colourless, crystalline, m. p. about  $190^\circ$ , reddening at about  $150^\circ$ ; *diphorone tin tetrachloride*, colourless crystals, m. p. about  $142^\circ$  (decomp.); *bisdimethylpyrone tin tetrachloride*, colourless crystals, m. p.  $232-235^\circ$  (decomp.); *dixanthone tin tetrachloride*, sandy-yellow powder, m. p.  $245^\circ$ ; *dibenzophenone tin tetrachloride*, colourless crystals; *bis-phenyl styryl ketone tin tetrachloride*, deep yellow crystals; *bis-distyryl ketone tin tetrachloride*, orange powder, m. p.  $188^\circ$  (decomp.); *bis-cinnamylidenacetophenone tin tetrachloride*, Bordeaux-red crystals, m. p. about  $160^\circ$  (decomp.); *bis-dicinnamylidenacetone tin tetra-*

chloride, black precipitate, decomp. below  $100^{\circ}$ ; *dibenzoylpiperidine tin tetrachloride*, colourless, crystalline, m. p. about  $213^{\circ}$ ; *dicinnamoylpiperidine tin tetrachloride*, colourless leaflets, m. p.  $221^{\circ}$ ; *dipiperine tin tetrachloride*, deep yellow crystals; *dipiperine tin tetrabromide*, deep yellow crystals, m. p.  $183^{\circ}$  (decomp.); *piperine stannichloride*,  $2C_{17}H_{19}O_3N.H_2SnCl_6$ , compact, yellow crystals (from alcohol containing hydrogen chloride); *piperine stannibromide*,  $2C_{17}H_{19}O_3N.H_2SnBr_6$ , compact, deep yellow crystals, m. p.  $182-184^{\circ}$  (decomp.); *piperine hydrochloride*,  $C_{17}H_{19}O_3N.HCl$ , canary-yellow, crystalline; *piperine dihydrochloride*,  $C_{17}H_{19}O_3N_2.2HCl$ , orange powder; *piperine hydrobromide*,  $C_{17}H_{19}O_3N.HBr$ , canary-yellow, crystalline, m. p. about  $170^{\circ}$ . Attempts to prepare a substance,  $2CPh_3Cl.SnCl_4$ , yield only Kebrmann's triphenylmethyl chloride tin tetrachloride,  $CPh_3Cl.SnCl_4$ .  
C. S.

**Modification of the Friedel and Crafts' Reaction Admitting of the Preparation of  $\alpha$ -Naphthyl Ketones to the Exclusion of the  $\beta$ -Isomerides.** E. CAILLE (*Compt. rend.*, 1911, 153, 393-394).—A solution of the acid chloride in carbon disulphide is cooled to  $0^{\circ}$ , and treated with aluminium chloride in small portions at a time; crystals separate, consisting of a compound of the ketone with aluminium chloride; after about twenty-four hours these are collected, and decomposed with ice-water acidified with hydrochloric acid. The resulting ketone consists entirely of the  $\alpha$ -naphthyl derivative, and the yield is 60-80%.  
W. O. W.

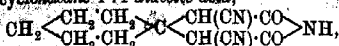
**2-Methyl-laurenone. A New Ketone Derived from Camphor.** RENÉ LOCQUIN (*Compt. rend.*, 1911, 153, 284-287. Compare Tie mann, Abstr., 1901, i, 5).—When the lactone,  $C_{10}H_{16}O_2$ , obtained by Baeyer and Villiger (Abstr., 1900, i, 133) in the oxidation of camphor with Caro's acid is heated with 20% phosphoric acid at  $190-200^{\circ}$ , it loses carbon dioxide and forms 2-methyl-laurenone (2:3:3:4-tetramethyl- $\Delta^1$ -cyclopentenone-5),  $\begin{matrix} \text{CMe}_2 \cdot \text{CHMe} \\ \text{CMe} = \text{CH} \end{matrix} > \text{CO}$ , b. p.  $82-86^{\circ}/10$  mm,

$95-96^{\circ}/18$  mm.,  $D_4^{20} 1.062$ . The constitution of this substance was established by its conversion by successive oxidation and esterification into ethyl  $\gamma$ -keto- $\alpha\beta$ -trimethylvalerate,  $\text{COMe} \cdot \text{CMe}_2 \cdot \text{CHMe} \cdot \text{CO} \cdot \text{Et}$ , b. p.  $105-107^{\circ}/12$  mm., which forms a semicarbazone, m. p.  $158-159^{\circ}$ , and on treatment in the usual way yields the corresponding trimethylsuccinic acid.

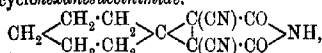
2-Methyl-laurenone forms two semicarbazones, m. p.  $150^{\circ}$  and  $198^{\circ}$  respectively, a normal oxime, m. p.  $95-96^{\circ}$ , b. p.  $122-128^{\circ}/10$  mm.; the phenylcarbamilidoxime has m. p.  $101-102^{\circ}$ . When treated with sodium and alcohol, it yields 1:2:2:3-tetramethyl-4-cyclopentanone,  $C_8H_{16}O$ ; the phenylurethane has m. p.  $113-114^{\circ}$ . 1:2:2:3-Tetramethyl-4-cyclopentanone, b. p.  $178-180^{\circ}$ , forms two semicarbazones, m. p.  $182^{\circ}$  and  $232^{\circ}$  respectively.  
W. O. W.

**Some New Derivatives of cycloHexanones.** ICILIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1911, 46, 662-669. Compare Abstr., 1901, i, 371; Thole and Thorpe, Trans., 1911, 89, 422).—The imide

of *αα*-dicyanocyclohexane-1:1-diacetic acid,



prepared from cyclohexanone and ethyl cyanoacetate, crystallises in colourless needles, m. p. 211–212°. The ammonium salt is the primary product. When treated with bromine water, the imide yields quantitatively an additive product containing two atoms of bromine, m. p. 164–165° (with evolution of bromine). This dibromide when heated on a water-bath with 50% formic acid until effervescence ceases yields *αβ*-dicyano-*αβ*-cyclohexanesuccinimide.



which crystallises in lustrous needles, m. p. 238–240°. The removal of bromine from the dibromide can also be effected by warming it in aqueous-alcoholic solution.

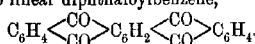
1-Methylcyclohexan-3-one yields similar products.

The imide of *αα*-dicyano-1-methylcyclohexane-3:3-diacetic acid,  $\text{CH}_2 \begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CH}_2 \end{array} \text{C} \begin{array}{c} \text{CH}(\text{CN}) \cdot \text{CO} \\ \text{CH}(\text{CN}) \cdot \text{CO} \end{array} \text{NH}$ , has m. p. 240–241° (becoming brown; on Maquenne block the m. p. is 244–245°). The ammonium salt crystallises well. The imide absorbs two atoms of bromine, and the dibromide yields *αβ*-dicyano-*αβ*-1-methylcyclohexane-3:3-succinimide,  $\text{CH}_2 \begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CH}_2 \end{array} \text{C} \begin{array}{c} \text{C}(\text{CN}) \cdot \text{CO} \\ \text{C}(\text{CN}) \cdot \text{CO} \end{array} \text{NH}$ , m. p. 241–242° (Maquenne block). R. V. S.

"Tagayasan," a Japanese Wood the Dust of which Causes Inflammation. K. IWAKAWA (*Arch. exp. Path. Pharm.*, 1911, 65, 315–324).—Workmen dealing with Tagayasan timber suffer from inflammation of the eyes. The active principle was extracted by means of benzene, and appears to be identical with chrysophano-hydroanthrone,  $\text{C}_{15}\text{H}_{12}\text{O}_3$  (compare Abstr., 1900, i, 42), which, however, had not hitherto been found to occur naturally. The pure substance causes the same symptoms as the wood dust. E. J. R.

Synthesis of Linear Diphthaloylbenzene. ERNST PHILIPPI (*Monatsh.*, 1911, 32, 631–635).—The anhydride of pyromellitic acid condenses with benzene in presence of aluminium chloride to a mixture of 4:6-dibenzoylisophthalic acid and 2:5-dibenzoyltetraphthalic acid. These are separated by making use of their solubility in water and nitrobenzene.

Both isomerides are converted on heating with concentrated sulphuric acid into linear diphthaloylbenzene,



4:6-Dibenzoylisophthalic acid crystallises in colourless needles or long plates, m. p. 263–264° (darkening).

2:5-Dibenzoyltetraphthalic acid crystallises in long, lanceolate plates or slender needles, which soften at 235°, m. p. 307–309°. On distillation with calcium oxide in a stream of hydrogen under reduced



pressure, *p*-dibenzoylbenzene is obtained; this confirms the constitution.

*Diphthaloylbenzene* crystallises in bunches of yellow needles, which are not altered at 370°, but sublime at a higher temperature. It forms a dark red vat with alkaline hyposulphite, and dyes cotton first green and then dark blue. E. F. A.

**New Method of Formation of Flavanthren.** ERWIN BENESCH (*Monatsh.*, 1911, 32, 447—456).—Flavanthren has been synthesised by the following series of reactions, starting from the methyl ether of 2-hydroxyanthraquinone, which is converted through the nitro- and amino-derivatives into 1-iodo-2-methoxyanthraquinone. This, when heated with copper powder, gives 2:2'-dimethoxy-1:1'-dianthraquinonyl, which after hydrolysis is converted by ammonia into 2:2'-diamino-1:1'-dianthraquinonyl; this last changes spontaneously into flavanthren.

On nitration of 2-methoxyanthraquinone, two isomeric mononitro-derivatives, m. p. 271° and 225°, are obtained. The less fusible isomeride does not form flavanthren, and is possibly 3-nitro-2-methoxyanthraquinone.

1-Nitro-2-methoxyanthraquinone forms yellow crystals, m. p. 271°.

3-Nitro-2-methoxyanthraquinone, m. p. 225°, is somewhat darker in colour and more soluble than the isomeride.

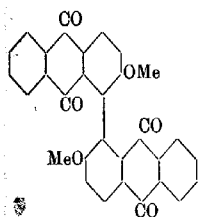
1-Amino-2-methoxyanthraquinone is red, and has m. p. 224°. The isomeric 3-amino-derivative has m. p. 218—222°.

\* 1-Iodo-2-methoxyanthraquinone forms lustrous, brown crystals, m. p. 265°. The 3-iodo-isomeride has m. p. 210—212°.

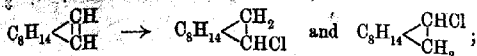
2:2'-Dimethoxy-1:1'-dianthraquinonyl (annexed formula) is a yellow powder, m. p. 346°. On hydrolysis by means of anhydrous aluminium chloride, 2:2'-dihydroxy-1:1'-dianthraquinonyl is obtained as a green, amorphous powder. The yields in these operations are but small, and flavanthren itself was not isolated, but its presence

was definitely characterised. E. F. A.

**Constitution of Camphene.** II. Camphene Hydrochloride and Camphene Hydrate. OSSIAN ASCHAN (*Annalen*, 1911, 383, 1—38. Compare Abstr., 1910, i, 709).—Since there are at present two competing formulæ, namely, the author's "ethylene" formula and Wagner's "methylene" formula, for camphene, the question of the individual nature of the terpene acquires great importance. The author attempts, admittedly without much success, to answer it by converting camphene (from various sources) through the hydrochloride into camphene hydrate, regenerating camphene therefrom, and comparing the physical properties of the regenerated and the original camphenes. In the course of his experiments, which include the examination of pinene hydrochloride and bornyl and isobornyl chlorides, the author obtains evidence which indicates that (1) crude



camphene hydrochloride is a mixture of two stereoisomerides,  $\alpha$  and  $\beta$ , derived from camphene ("ethylene" formula), thus:



2)  $\alpha$ -camphene hydrochloride, which is not decomposed by dilute aqueous potassium hydroxide, is the main constituent of bornyl chloride, whilst  $\beta$ -camphene hydrochloride is the chief constituent of isobornyl chloride.

Thus camphene (prepared from the hydrochloride of rectified American turpentine), b. p. 159.5—160°, m. p. 40.5—41.5°, and  $[\alpha]_D^{20} + 12.85^\circ$  in benzene, is converted by ethereal hydrogen chloride into crude camphene hydrochloride, m. p. 137—140°, and  $[\alpha]_D - 6.40^\circ$ . This hydrochloride in benzene is shaken with dilute (approximately 3%) aqueous potassium hydroxide for twelve hours at 60°, and again for twelve hours at 80—90° after the addition of more potassium hydroxide, whereby is obtained camphene hydrate (from the  $\alpha$ -camphene hydrochloride), b. p. 206—207.5°, m. p. 149°,  $[\alpha]_D - 2.89^\circ$  in benzene, together with some camphene (from the  $\beta$ -camphene hydrochloride), b. p. 159.5—160.5°, m. p. 43—44°,  $D_4^{20} 0.8573$ ,  $[\alpha]_D^{20} + 10.92^\circ$  in benzene. When boiled with acetic anhydride and sodium acetate, the camphene hydrate yields, together with a little isobornyl acetate, a camphene, b. p. 159—161°, m. p. 44—45°,  $[\alpha]_D^{20} + 12.63^\circ$  in benzene,  $D_4^{20} 0.8531$ , and  $n_D^{20} 1.45952$ . Finally, the camphene hydrate in benzene is converted by hydrogen chloride into the original camphene hydrochloride, m. p. 151—153.5° (after recrystallisation from methyl alcohol containing hydrochloride), and  $[\alpha]_D^{20} - 6.495^\circ$  in benzene. (Camphene hydrate would be expected to form only  $\alpha$ -camphene hydrochloride; probably the hydrogen chloride acts as a dehydrating agent, producing camphene, which then unites with the acid to form the mixture of  $\alpha$ - and  $\beta$ -camphene hydrochlorides.) The fact that the two camphenes, obtained in the preceding transformations agree very closely with the original camphene in physical properties indicates that the terpene is an individual substance.

Similar results have been obtained with a camphene (from Siberian pine-needle oil), b. p. 159—159.5°, m. p. 47—48°,  $D_4^{20} 0.8548$ , and  $[\alpha]_D^{20} - 89.29^\circ$ . A liquid portion of the camphene, b. p. 159—160°,  $D_4^{20} 0.8728$ , and  $[\alpha]_D - 75.96^\circ$ , is converted into the hydrochloride, m. p. 137° (crude) and 149—150° (recryst. from benzene), and  $[\alpha]_D^{20} 47.33^\circ$  in benzene, which yields by hydrolysis with dilute potassium hydroxide at 60°, and finally at 80°, camphene hydrate,  $[\alpha]_D - 1.35^\circ$  in benzene, from which sodium acetate and boiling acetic acid regenerate a camphene, b. p. 161—163°, m. p. 49.5—51°, and  $[\alpha]_D^{20} - 76.04^\circ$  in benzene.

When hydrolysed by dilute potassium hydroxide under the preceding conditions, bornyl chloride (from the *l*-borneol of Siberian pine-needle oil) yields camphene hydrate, m. p. 148—149°, and a trace of camphene, whilst isobornyl chloride (from technical isoborneol) yields camphene, b. p. 159—160°, m. p. 50—51°,  $[\alpha]_D^{20} - 0.45^\circ$  in benzene, and a trace of camphene hydrate. This evidence is the reason for statement (2) above.

Pinene hydrochloride (from American turpentine), m. p.  $126^{\circ}$ ,  $[\alpha]_D^{20}$   $6.55^{\circ}$ , is scarcely attacked by 2% potassium hydroxide below  $100^{\circ}$ , but is hydrolysed by a mixture of alcohol, benzene, and milk of lime at  $135^{\circ}$  and finally at  $150^{\circ}$ , yielding 7–9% of camphene, b. p.  $159.5$ – $161^{\circ}$ , m. p.  $40$ – $41^{\circ}$ ,  $[\alpha]_D^{20}$   $+14.52^{\circ}$  in benzene, and less than 40% of camphene hydrate, b. p.  $206$ – $206.5^{\circ}$ , m. p.  $149$ – $150^{\circ}$ ,  $[\alpha]_D^{20}$   $-3.24^{\circ}$  in benzene; the camphene obtained from the hydrate by acetic anhydride and potassium acetate has b. p.  $159.5$ – $160^{\circ}$ , m. p.  $43$ – $44^{\circ}$ ,  $D_4^{20}$   $0.8542$ , and  $[\alpha]_D^{20}$   $+15.43^{\circ}$  in benzene. Similar results are obtained with a strongly active pinene hydrochloride (from Grecian turpentine), m. p.  $128$ – $130^{\circ}$ , and  $[\alpha]_D^{20}$   $+28.88^{\circ}$  in benzene; the camphene hydrate obtained therefrom has m. p.  $149$ – $150^{\circ}$  and  $[\alpha]_D^{20}$   $-21.79^{\circ}$  in benzene, and yields camphene, b. p.  $159$ – $160^{\circ}$ , m. p.  $44$ – $45^{\circ}$ , and  $[\alpha]_D^{20}$   $+85.68^{\circ}$  in benzene. There is no doubt, therefore, that the camphene hydrate from pinene hydrochloride is identical with that from camphene hydrochloride.

The higher fractions of the products of the preceding hydrolyses contain chlorine, showing that crude camphene hydrochloride, bornyl chloride, and isobornyl chloride contain a third constituent which is unattacked by 3% potassium hydroxide at  $60$ – $80^{\circ}$ ; it is also resistant to aniline at the ordinary temperature, but is hydrolysed by hot aniline and by alcoholic potassium hydroxide.

Attempts to separate the  $\alpha$ - and the  $\beta$ -forms of camphene hydrochloride by crystallisation from petroleum have yielded the less soluble and more stable  $\alpha$ -modification, which has m. p.  $150$ – $151^{\circ}$  in its racemic form and  $157$ – $158^{\circ}$  in its strongly active form (that from *l*-bornyl chloride). The presence of the  $\beta$ -modification in crude camphene hydrochloride and also in bornyl and isobornyl chlorides is indicated by the rate of hydrolysis of these chlorides by alcoholic potassium hydroxide; the results are expressed graphically.

Camphene hydrate is converted almost quantitatively into isobornyl acetate by heating with sulphuric and acetic acids and a little water at  $60$ – $70^{\circ}$ .  
C. S.

**Constitution of Camphene. III. Individuality of Camphene from Various Sources.** OSSIAN ASCHAN (*Annalen*, 1911, 383, 39–51. Compare preceding abstract).—Samples of camphene from seven different sources have been oxidised by potassium permanganate essentially by the process described previously (Abstr., 1910, i, 709), and the products have been separated into their constituents (camphenilone, camphene glycol, camphenilic acid, sodium salt of an acid, m. p.  $138^{\circ}$ , camphenic acid, and other acids soluble in water) always under exactly the same conditions, so that the quantities of each constituent are comparable. It is found in all seven cases that the quantities of the chief oxidation products are, in general, nearly the same, and that the quantities of camphenilic acid and camphenic acid stand in a definite ratio to one another, 1:10. These results not only indicate that camphene is an individual substance, but also furnish strong evidence in favour of the author's "ethylene" formula. If camphene has Wagner's "methylene" formula, the formation of the chief oxidation product, camphenic acid, must be explained by

assuming an intramolecular change, whereby a five-membered ring becomes a six-membered ring. On the other hand, accepting the "ethylene" formula of camphene, the formation of camphenic acid is a direct process, and the production of the relatively small amount of camphenilic acid (and also of camphenilone and camphene glycol) is explicable by the more rational assumption of the change of a six-membered to a five-membered ring.

C. S.

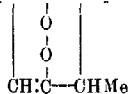
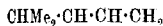
**Constitution of Camphene. IV. Stereoisomeric Camphenic Acids.** OSSIAN ASCHAN (*Annalen*, 1911, 383, 52—68. Compare preceding abstracts).—*cis-dl*-Camphenic acid is partly transformed into *trans-dl*-camphenic acid,  $C_8H_{14}(CO_2H)_2$ , m. p. 122—123° (*diamide*, m. p. 231—232°; *dianilide*, m. p. 165°), by distillation under 5 mm. pressure, or by heating for twelve hours at 180° with equal parts of acetic acid and 38% hydrochloric acid; the two modifications are separated by alcoholic sodium ethoxide, the sodium salt of the *trans*-acid being the more soluble. The two modifications in approximately equal amounts are also obtained by the reduction of *cis-a*-bromocamphenic acid by zinc and acetic and hydrochloric acids.

The conversion of *cis*-camphenic acid in a normal way into the *trans* modification is important, since it furnishes a fairly certain proof that the migrating carboxyl group is attached to a ring carbon atom.

The distillation of *cis*-camphenic acid under ordinary pressure yields products which are receiving further examination.

C. S.

**Chemical Investigation of the Oil of Chenopodium.** E. K. NELSON (*J. Amer. Chem. Soc.*, 1911, 33, 1404—1412).—This oil is obtained by distillation of *Chenopodium ambrosioides* var. *Anthemintica*. It contains about 70% of ascaridole (Abstr., 1908, i, 667), b. p. 96—97°/8 mm.,  $D_{20}^{25}$  0.9985,  $n_D^{20}$  1.4769,  $\alpha_D^{20}$  +0.7°. [The pure compound may be optically inactive, and this slight activity may be due to a trace of *d*-camphor (see below)]. Ascaridole readily undergoes rearrangement to form a glycol anhydride analogous to pinene oxide, a change indicating that it is an unstable dioxide. Further evidence is afforded by



its property of exploding when heated, and by the violence of its reaction with ferrous sulphate and other reagents. The annexed constitution is assigned to it.

The author prepared *ascaridole glycol* (b. p. 271—272°, m. p. 62.5—64°,  $D_{20}^{25}$  1.0981,  $n_D^{20}$  1.4796,  $\alpha_D^{20}$  0) by treatment with ferrous sulphate, also the *monobenzoate*, m. p. 136—137°, and the *diobenzoate*, m. p. 116.5—117.5°, of the glycol.

An old sample of the oil was found to contain *d*-camphor.

E. J. R.

**Dithiocamphorcarboxylic Acid.** LÉO TCHUGAEFF and G. PROCOULEWSKY (*Compt. rend.*, 1911, 153, 388—390).—This substance was obtained in an unsuccessful attempt to prepare a xanthate of the

camphor series. Sodium camphor, prepared by means of sodamide, was treated successively with carbon disulphide and methyl sulphate. After heating on the water-bath, the mixture gave *methyl dithio-*

*camphorcarboxylate*,  $C_8H_{14} \begin{smallmatrix} CH \cdot CS_2Me \\ \diagdown \\ CO \end{smallmatrix}$ , as a deep yellow oil, b. p. 179°

8 mm.,  $D_{20}^{25} 1.1204$ ,  $[a]_D +42.58^\circ$ . The substance is remarkably stable, and has b. p. about 300° under ordinary pressure, practically without decomposition. Alcoholic potassium hydroxide converts it into potassium camphorcarboxylate. *Dithiocamphorcarboxylic acid* is a yellow oil, decomposing on heating into camphor and carbon disulphide. The *copper salt* is deep brown.

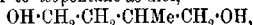
W. O. W.

**Decomposition of Terpenoid Substances by Glowing Metallic Wires.** CARL D. HARRIES and KURT GOTTLÖB (*Annalen*, 1911, 383, 228—229).—An apparatus, termed the "isoprene lamp," is figured and described. A coil of platinum wire, 120 cm. in length and resistance 9Ω at an average red heat, is suspended in the neck of a flask and heated electrically (about 5 amperes at 220 volts). The flask is provided with a vertical condenser containing water at 50°. The liquid in the flask is gently boiled; the undecomposed vapour is condensed and returns to the flask, whilst the volatile decomposition products escape, and are condensed by a freezing mixture. Commercial *r*- or *l*-pinene yields only about 1% of isoprene, whilst commercial *carvone* yields 30—50%, according to the amount of limonene it contains.

C. S.

**Butadienes and Some Synthetic Caoutchouc Obtained Therefrom.** CARL D. HARRIES (*Annalen*, 1911, 383, 157—227).—The older processes for the synthesis of isoprene are condemned either on account of the rarity of the initial material, or because the resulting isoprene is contaminated with trimethylethylene or *as*-dimethylallene. The following process is adopted to obtain pure isoprene in quantity sufficient for the determination of its physical constants.

[With KARL NERESHEIMER.]—Ethyl pyrotartrate is reduced by sodium and alcohol to *isopentane-αδ*-diol,



b. p. 124—125°/13 mm.,  $D_{20}^{25} 0.9954$ ,  $n_D^{20} 1.45173$  (*diacetate*, b. p.

116—117°/17 mm.,  $D_{20}^{25} 1.0434$ ,  $n_D^{20} 1.42717$ ; *oxide*,  $\begin{smallmatrix} CHMe \cdot CH_2 \cdot O \\ | \\ CH_2 - CH_2 \end{smallmatrix}$ ).

b. p. 86—87°,  $D_{20}^{25} 0.8643$ ,  $n_D^{20} 1.41122$ ; *s*-diphenyldiurethane, m. p. 97°; *tetraphenyldiurethane*, m. p. 102°. The glycol is converted by 60% hydrobromic acid at 100° into *αδ*-dibromo-β-methylbutane (Abstr., 1907, i, 743), b. p. 84—86°/11 mm.,  $D_{20}^{25} 1.6986$ ,  $n_D^{20} 1.51217$ , which reacts with 33% alcoholic trimethylamine at 100° to form the corresponding bis-quaternary ammonium bromide, the base of which, by distillation, yields isoprene (in 50% yield), b. p. 36—37°,  $D_{20}^{25} 0.6804$ ,  $D_{20}^{25} 0.6793$ ,  $n_D^{20} 1.42267$ ,  $n_D^{20} 1.41807$ ,  $n_D^{20} 1.44340$ .

For the technical preparation of isoprene, Hofmann's (Elberfeld)

process, with ~~the~~ ~~cresol~~ is recommended as giving very pure isoprene. The author obtains most of his (pure) isoprene by heating turpentine or, better, dipentene or limonene over a glowing platinum spiral (preceding abstract), but also obtains a fair amount by dropping  $\beta$ -dibromo- $\beta$ -methylbutane (obtained from acetone through the amyl alcohol) on soda-lime at 600°. The soda-lime is advantageously previously saturated with carbon dioxide (the reagent thus prepared is more porous than calcium carbonate or similar substances), and the process, for which a special apparatus has been designed, is applicable to the preparation of other homologous hydrocarbons. When heated with quinoline,  $\beta$ -dibromo- $\beta$ -methylbutane is converted into a substance, b. p. 39–40°,  $D_4^{20}$  0.6719,  $n_D^{20}$  1.40188, which probably consists chiefly of *as*-dimethylallene.

Erythrene ( $\Delta^v$ -butadiene) is conveniently obtained from phenol by the Elberfeld process. A satisfactory laboratory method starts from *sec*-butyl alcohol. This is converted by phosphoric oxide into the olefine, the dibromide of which yields butadiene by the hot soda-lime process.

$\beta$ -Dimethyl- $\Delta^v$ -butadiene can be obtained by the author's method with pinacone hydrochloride and hot soda-lime, but is best prepared from pinacone and potassium hydrogen sulphate by the Elberfeld process.

Each of the preceding butadienes yields by suitable polymerisation a "normal" caoutchouc and a "sodium" caoutchouc, which are similar in appearance, but differ in their behaviour with ozone.

"Normal" caoutchoucs are obtained when the polymerisation is effected by the acetic acid process or, better, by heat alone, as in the Elberfeld method. Experiments with "normal" isoprene caoutchouc show that in order to secure a product of good quality it is necessary, not only to use pure isoprene, but also to exclude oxygen during the process of polymerisation. Synthetic caoutchoucs are very sensitive to autoxidation, and the higher the temperature of polymerisation, the more readily does the caoutchouc undergo autoxidation.

The quality of a synthetic caoutchouc is conveniently tested by submitting the caoutchouc to a process of cold vulcanisation (the hot process requires costly apparatus and a large amount of material, and is unsuitable for laboratory experiments), and examining the solidity and elasticity of the product. As tested by this method, the best synthetic caoutchouc is produced when isoprene is polymerised by heat alone at the lowest possible temperature.

The comparison of synthetic with natural caoutchouc is very difficult, because only the nitrosites and tetrabromides are available for comparative purposes, and these compounds are amorphous, difficult to purify, and have no definite m. p. The author, therefore, prefers to rely on a comparison of the ozonides and of their products of decomposition. He thus finds that "normal" isoprene caoutchouc (and, still more distinctly, "normal" dimethylbutadiene caoutchouc) must contain a small amount of another caoutchouc, because the decomposition products of its ozonide contain some substances (methylglyoxal ?) which are not found among the products of decomposition of the ozonide

or natural caoutchouc. Moreover, a small portion of the synthetic caoutchouc is very much more difficultly ozonised than is natural caoutchouc.

The constitution  $\left[ \text{CMe} \begin{array}{c} \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH} \cdot \text{CH} \cdot \text{CH}_2 \end{array} \text{CHMe} \right]_x$  or  $\left[ \text{CMe} \begin{array}{c} \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH} \cdot \text{CH} \cdot \text{CHMe} \end{array} \text{CH}_2 \right]_x$

is suggested for the second synthetic caoutchouc.

A comparison of "normal" isoprene caoutchouc and purified Para caoutchouc with regard to their behaviour with Budde's brominating solution shows that hydrogen bromide is more copiously evolved during the reaction of the synthetic caoutchouc, and that the resulting tetrabromide is easily and completely soluble in carbon disulphide.

The action of nitrous fumes on "normal" isoprene caoutchouc yields, as in the case of natural caoutchouc, a yellowish-green, insoluble nitrosite "a," decomp. 115–120° or 130–135°, and a soluble nitrosite "c," decomp. 158–162°, the composition of which approximates to the formula  $\text{C}_{10}\text{H}_{15}\text{O}_7\text{N}_3$  less exactly than does that of the nitrosite "c" of carefully purified natural caoutchouc, which also has decomp. 158–162°. When distilled in a vacuum, the synthetic caoutchouc behaves like natural rubber, and so also when treated with ozone (with the two reservations mentioned above).

When heated in glacial acetic acid at 110–120° for ten days,  $\Delta^{\gamma}$ -butadiene yields "normal" butadiene-caoutchouc,  $(\text{C}_8\text{H}_{12})_x$ , a pure product being obtained when oxygen is excluded during the polymerisation. This caoutchouc resembles gelatin, is non-elastic and easily torn, and is sparingly soluble except in chloroform. It forms a yellow, amorphous, easily soluble nitrosite, decomp. above 80°, and yields an explosive, oily ozonide (in chloroform), or a white, solid ozonide (in carbon tetrachloride), the latter closely resembling the ozonide of  $\Delta^{1:3}$ -cyclooctadiene. When polymerised by heat alone, butadiene yields a solid, the distillation of which at 100–110°/0 mm. furnishes a hydrocarbon,  $\text{C}_8\text{H}_{12}$ , b. p. 36°/23 mm.,  $D_4^{20}$  0.8523,  $n_D^{20}$  1.46768, which resembles the terpenes. The residue contains the caoutchouc, which is quite similar to that obtained by the acetic acid process, except that it is insoluble even in chloroform, and is unaffected by nitrous acid or ozone.

Dimethylbutadiene polymerises very much more slowly than isoprene. The acetic acid process yields a yellow, friable product. When heated in a sealed tube at 100° for about twenty-three days, dimethylbutadiene is converted into a viscous mass, which is distilled at ordinary pressure to remove the unchanged hydrocarbon, and then at 110°/0 mm. to separate the small amount of terpene by-product. An ethereal solution of the residue yields, by the addition of alcohol, "normal" dimethylbutadiene-caoutchouc,  $(\text{C}_{12}\text{H}_{20})_x$ , which can scarcely be distinguished from isoprene caoutchouc in its external appearance. It can be vulcanised, and forms a tetrabromide,  $\text{C}_{12}\text{H}_{20}\text{Br}_4$ , evolving hydrogen bromide at about 130°, and a nitrosite,  $\text{C}_{12}\text{H}_{19}\text{O}_2\text{N}_3$ , darkening at 120°. When ozonised in carbon tetrachloride, it gives a mixture of two ozonides, the decomposition of which by hot glacial acetic acid yields acetonylacetone and other substances which reduce Fehling's solution.

"Sodium" butadiene-caoutchouc,  $(\text{C}_8\text{H}_{12})_x$ , is obtained almost quantitatively when  $\Delta^{\gamma}$ -butadiene is heated with a little sodium wire in a sealed

tube at 35–40° for three hours, and the resulting viscous, brown mass is washed with dilute alcohol. When freshly prepared, it is pale yellow, transparent, and soluble in ether, chloroform, and benzene, but it loses these properties after keeping, and becomes viscous and stringy. It can be vulcanised (hot or cold process), yielding a product which surpasses all other synthetic caoutchoucs in elasticity. The *nitrosite* (approximately  $C_8H_{12}O_3N_2$ ) and *bromide* (approximately  $C_8H_{12}Br_4$ ) are described. In chloroform, 6–7% ozone produces an impure, oily *diozonide*,  $C_8H_{12}O_6$ , whilst 12–14% ozone produces a very explosive substance, which is apparently an ozonide,  $C_8H_{12}O_4$ ; the decomposition products of these substances are being examined.

"Sodium" *isoprene-caoutchouc*,  $(C_{10}H_{16})_x$ , is obtained almost quantitatively by heating pure isoprene with sodium at 60° for about fifty hours. It resembles the "normal" caoutchouc in its physical properties (except appearance), but is more soluble. It can be vulcanised, forms a white *tetrabromide* very similar to the "normal" *tetrabromide*, and yields with nitrous acid a mixture of two *nitrosites*, one insoluble, the other soluble; the latter is a yellowish-white powder, darkening at 170–180°. The "sodium" caoutchouc in carbon tetrachloride is attacked very slowly by 12–14% ozone, and yields a mixture of an ozonide and diozonide. With 6–7% ozone in chloroform, it forms a solid *diozonide*,  $C_{10}H_{16}O_6$ , which is quite different from the diozonide of ordinary caoutchouc, since its products of decomposition do not give the pyrrole reaction, and do not contain any characteristic substance except a very small amount of levulaldehyde.

"Sodium" *dimethylbutadiene-caoutchouc*, obtained by heating dimethylbutadiene with sodium at 60° for ten to twelve days and nights, forms, after purification, a mass like gutta-percha. Its behaviour with ozone is similar to that of "sodium" isoprene caoutchouc; evidence of the presence of the "normal" caoutchouc is also obtained. The *tetrabromide* is a white powder, which evolves hydrogen bromide at 130°; the *nitrosite* is also described.

The paper concludes with some remarks on the constitution of natural caoutchouc and a reply to Pickles' criticisms (*Trans.*, 1910, 97, 1085).

C. S.

Chemistry of Caoutchouc. II. Physico-chemical Investigation of the Extraction of Resin. DAVID SPENCE and J. H. SCOTT (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 83–85. Compare this vol., i, 657).—Measurements have been made of the quantities of resin extracted from caoutchouc by boiling acetone during successive equal intervals of time. When the percentage of extracted resin is plotted against time, a curve is obtained which closely resembles the corresponding curve representing Bayliss's data for the rate of extraction of salts from gelatin by water. From this, it appears probable that a portion, at least, of the resin is present in the caoutchouc in the adsorbed condition.

Reference is made to the extraction experiments of Zilchert (*Gummi Zeit.*, 1911, 25, 716), in which different kinds of caoutchouc were examined. The differences met with are supposed by the authors to



be due to differences in the degree of dispersity of the colloidal system.

H. M. D.

**New Synthetic Glucosides.** EMIL FISCHER and BURKHARDT HELFERICH (*Annalen*, 1911, 383, 68—91. Compare Abstr., 1910, i, 716).—With the object of obtaining as many synthetic glucosides as possible for comparison with natural products, the authors have applied König and Knorr's process to geraniol, cyclohexanol, benzyl alcohol, cetyl alcohol, and ethyl glycolate. In every case except the last two the glucosides are split by emulsin, and therefore belong to the  $\beta$  series; there is no doubt that the two exceptions also belong to the same series. The same method is used for each alcohol, except in the case of ethyl glycolate, where a solvent is not employed. The alcohol and bromoacetoglucose dissolved in ether are shaken for several hours with freshly prepared dry silver oxide until a filtered sample no longer gives a precipitate of silver bromide when boiled with aqueous silver nitrate.

*Tetra-acetyl- $\beta$ -benzyl-d-glucoside*,  $\text{CH}_3\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{O}_5\text{Ac}_4$ , white needles, m. p. 96—101° (corr.), has  $[\alpha]_D^{20} = -49.51^\circ$  in alcohol, and is hydrolysed by aqueous barium hydroxide to  *$\beta$ -benzyl-d-glucoside*,

$\text{CH}_3\text{Ph}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}_5$ , flexible needles, m. p. 123—125° (corr.),  $[\alpha]_D^{20} = -55.76^\circ$  in water, which has a very bitter taste, does not reduce Fehling's solution, and is rapidly hydrolysed by dilute hydrochloric acid or emulsin.

*Tetra-acetyl- $\beta$ -cyclohexyl-d-glucoside*,  $\text{C}_6\text{H}_{11}\cdot\text{C}_6\text{H}_4\cdot\text{O}_5\text{Ac}_4$ , long needles, m. p. 120—121° (corr.),  $[\alpha]_D^{20} = -29.74^\circ$  in alcohol, yields  *$\beta$ -cyclohexyl-d-glucoside*,  $\text{C}_6\text{H}_{11}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}_5$ , m. p. 133—137° (corr.),  $[\alpha]_D^{20} = -41.55^\circ$  in water, by hydrolysis as above. *Tetra-acetyl- $\beta$ -geranyl-d-glucoside*,  $\text{C}_{10}\text{H}_{17}\cdot\text{C}_6\text{H}_4\cdot\text{O}_5\text{Ac}_4$ , white needles, m. p. 29—30°,  $[\alpha]_D^{20} = -25.17^\circ$  in alcohol, is hydrolysed by aqueous alcoholic barium hydroxide, yielding  *$\beta$ -geranyl-d-glucoside*,  $\text{C}_{10}\text{H}_{17}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}_5$ , long needles, m. p. 58°,  $[\alpha]_D^{20} = -38.12^\circ$  in water. *Tetra-acetyl- $\beta$ -cetyl-d-glucoside*,

$\text{C}_{16}\text{H}_{33}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}_5\text{Ac}_4$ , glistening needles, m. p. 71—73° (corr.),  $[\alpha]_D^{20} = -20.19^\circ$  in alcohol, is not attacked by dilute hydrochloric or sulphuric acid, and is hydrolysed by boiling alcohol and 10% sodium hydroxide, yielding  *$\beta$ -cetyl-d-glucoside*,  $\text{C}_{16}\text{H}_{33}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}_5$ , colourless needles,  $[\alpha]_D^{20} = -22.02^\circ$  in alcohol, which is tasteless, melts indefinitely between 110° and 145°, is not attacked by Fehling's solution, by dilute mineral acids, or by emulsin, but is hydrolysed on the water-bath by acetic acid containing a few drops of hydrochloric acid. *Ethyl tetra-acetyl- $\beta$ -d-glucosidoglycollate*,  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}_5\text{Ac}_4$ , colourless needles, m. p. 83—84° (corr.),  $[\alpha]_D^{20} = -40.62^\circ$  in alcohol, is hydrolysed by N/5-barium hydroxide in twenty hours, yielding  *$\beta$ -d-glucosidoglycollic acid*,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}_5$ , clusters of stout leaflets, m. p. 165—167°,  $[\alpha]_D^{20} = -44.11^\circ$  in water, which has an acid taste, is not attacked by Fehling's solution or emulsin, and forms amorphous calcium, barium, zinc, lead, and mercury salts, and a crystalline sodium salt.  *$\beta$ -d-Glucosidoglycollamide*,  $\text{NH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}_5$ , obtained by saturating with ammonia a methyl-alcoholic solution of ethyl tetra-acetylglucosidoglycollate in a freezing mixture, has m. p. 167° (corr.)

nd  $[\alpha]_D^{25} = 43.24^\circ$  is hydrolysed by boiling dilute hydrochloric acid or by emulsin, and has a sweet taste and bitter after-taste; attempts to prepare the corresponding nitrile by boiling acetic anhydride result in the formation of *penta-acetylglucosidoglycollamide*,  $C_{18}H_{25}O_{12}N$ , white needles, m. p.  $146-149^\circ$  (corr.).

Pentabenzoyldextrose ( $[\alpha]_D^{20} + 25.40^\circ$  in chloroform) reacts like penta-acetyldextrose with hydrogen bromide in glacial acetic acid, forming *mono- $\beta$ -benzoglucose*,  $C_6H_7O_5BzBr$ , white needles, m. p.  $125-128^\circ$  (corr.),  $[\alpha]_D^{19} + 145.1^\circ$  in toluene, which interacts with methyl alcohol and silver oxide to produce *tetrabenzoyl- $\beta$ -methyl-d-glucoside*,  $CH_3 \cdot C_6H_7O_5Bz_4$ , white needles, m. p.  $160-162^\circ$  (corr.),  $[\alpha]_D^{20} + 30.99^\circ$  in chloroform; the last substance is converted into  $\beta$ -methylglucoside by shaking with alcoholic sodium ethoxide. C. S.

**The Glucoside of Leaves of the Pear Tree, its Presence in the Leaves of Different Varieties, its Detection in the Trunk and Root.** ÉMILE BOURQUELOT and (Mlle.) A. FICHTENHOLZ (*Compt. rend.*, 1911, 153, 468—471. Compare Abstr., 1910, i, 273; ii, 742).—Arbutin has been obtained from the leaves of four new varieties of pear tree in addition to those already studied. Probably all varieties of *Pirus* contain arbutin. This glucoside also occurs in the trunks and roots of the trees. W. O. W.

**Bile Pigments. I.** HANS FISCHER (*Zeitsch. physiol. Chem.*, 1911, 73, 204—239).—Maly's hydrobilirubin and the urobilin described by Garrod and Hopkins (Abstr., 1896, 1, 712) are shown to be mixtures. Hæmopyrrole is not the urobilinogen of the urine; the urobilin prepared from hæmopyrrole has quite different properties from that of urine.

Bilirubin dissolves to form colloidal solutions in presence of taurocholic and glycocholic acids. When reduced by means of sodium amalgam, bilirubin forms *hemibilirubin*,  $C_{16}H_{22}O_5N_2$  or  $C_{16}H_{20}O_5N_2$ , crystallising in short, colourless prisms, which tend to become red and belong to the monoclinic system [ $a : b : c = 1.8 : 1 : 0.7$ ;  $\beta = 110^\circ 20'$ ], m. p.  $192^\circ$  (decomp.). It gives an intense red coloration with sodium hydroxide and copper sulphate, forms dyes with diazonium salts, and changes on exposure to the air, first to a reddish-orange dye and then to a brown dye with a green surface reflex: these show all the urobilin reactions.

A new biliary acid, *lithocholic acid*,  $C_{24}H_{40}O_5$ , is isolated from ox gall stones. This crystallises in long prisms, m. p.  $184-186^\circ$  (corr.),  $[\alpha]_D^{20} + 32.14^\circ$ ; it is tasteless, and crystallises from acetic acid without a molecule of the solvent.

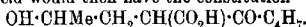
The composition of coprosterol given by Bondzynski and Humnicki is confirmed; this has m. p.  $112-116^\circ$ ,  $[\alpha]_D^{20} + 24.53^\circ$ .

Deoxycholic acid was obtained from fæces in colourless needles, m. p.  $145^\circ$ ,  $[\alpha]_D^{20} + 53.38^\circ$ . E. F. A.

**Hypericin (Hypericum Red).** C. ČERNÝ (*Zeitsch. physiol. Chem.*, 1911, 73, 371—382. Compare Wolff, *Pharm. Centr.-h.*, 1875, 16, 193).—The flowers of *Hypericum perforatum* contain a brilliant red

pigment in addition to a yellow pigment. The red colouring matter has an absorption spectrum very similar to that of oxyhaemoglobin. About 1 gram of pigment has now been isolated from 2470 grams of dried flowers having approximately the formula  $C_{18}H_{10}O_5$ ; the possibility of it being a flavone dye is suggested. Solutions of hypericin in organic solvents are blood-red; on dilution they become somewhat violet, and show a fire-red fluorescence. Measurements have been made of the absorption spectrum under various conditions in extension of those of Wolff (*loc. cit.*).  
E. F. A.

**Constitution of Divalolactone.** SIMA M. LOSANITSCH (*Compt. rend.*, 1911, 153, 390—392).—Fittig (Abstr., 1890, 286) regarded divalolactone, the product of the action of sodium ethoxide on valerolactone, as an ether containing two lactic oxygen atoms. The present author believes the third atom of oxygen to be ketonic, and the substance to have the formula 
$$\begin{array}{c} \text{CO} \text{---} \text{CH} \text{---} \text{CO} \cdot \text{C}_4\text{H}_7 \\ | \qquad \qquad | \\ \text{O} \cdot \text{CHMe} \cdot \text{CH}_2 \end{array}$$
 Fittig's divalolactonic acid would then have the constitution

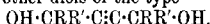


The following observations support these conclusions: Magnesium methyl iodide acts on valerolactone, giving *β*-dihydroxy-β-methyl-hexane, b. p. 121°/14 mm., whereas divalolactone does not give the analogous diol, but loses water, forming *dimethylanhydrovalolactone*,  $C_{12}H_{20}O_2$ , b. p. 104—105°/13.5 mm. This is a ketone, since on further treatment with magnesium methyl iodide, it yields a compound,  $C_{18}H_{24}O_2$ , b. p. 136—137°/13 mm., whilst the analogous ether, 2:5:5-trimethyltetrahydrofuran, b. p. 102—103°, does not react with the Grignard reagent. On treating divalolactonic acid with methyl sulphate and sodium hydroxide, it yields, according to conditions, the corresponding methyl ester, b. p. 114°/13 mm., or divalolactone.

The  $C_4H_7$  group in these compounds is under investigation.

W. O. W.

**Catalytic Preparation of Substituted Ketohydrofurans.** GEORGES DUPONT (*Compt. rend.*, 1911, 153, 275—277. Compare this vol., i, 554).—The conversion of dimethyl-Δ<sup>7</sup>-hexinene-β-diol into a tetrahydrofuran derivative by the catalytic action of mercuric sulphate has been extended to other diols of the type



When R and R' are saturated and of low molecular weight, the change is rapid and quantitative, but secondary reactions intervene when the radicals are unsaturated, aromatic, or of high molecular weight.

The following diols are new: *Acetylenediisovaleraldehyde*,  $\text{CH}_2 \cdot \text{CH} \cdot \text{CH}(\text{OH}) \cdot \text{C} \cdot \text{C} \cdot \text{CH}(\text{OH}) \cdot \text{CH} \cdot \text{CH}_3$ , b. p. 146°/15 mm.,  $D_{20}^{25} 1.0341$ ,  $n_D^{20} 1.5040$ ; *acetylenedicrotonaldehyde*,  $\text{CHMe} \cdot \text{CH} \cdot \text{CH}(\text{OH}) \cdot \text{C} \cdot \text{C} \cdot \text{CH}(\text{OH}) \cdot \text{CH} \cdot \text{CHMe}$ , m. p. 90—92°; the *tetrabromide* has m. p. 137°; *acetylenediisovaleraldehyde*,  $\text{CH}_2 \cdot \text{CH} \cdot \text{CH}(\text{OH}) \cdot \text{C} \cdot \text{C} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{Pr}^2$ , b. p. 158—160°/15 mm.,  $D_{20}^{25} 0.92475$ ,  $n_D^{20} 1.4614$ ; *acetylenedibutyrono*,  $\text{OH} \cdot \text{CPr}_2 \cdot \text{C} \cdot \text{C} \cdot \text{CPr}_2 \cdot \text{OH}$ , pearly spangles, m. p. 120°.

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3-Keto-2:5-dimethyltetrahydrofuran has b. p. 143°,  $D^{25}_D$  0.9894,  $n_D$  1.4267; the compound,  $C_6H_6(SO_4Hg_2O)$ , was isolated as an intermediate product in its formation. Pinacone gives a similar compound,  $C_6H_{10}(SO_4Hg_2O)$ , when treated with Denigès' reagent. The new ketone reduces Fehling's solution, and gives a semicarbazone, m. p. 168—170°. 3-Keto-2:5-dimethyl-2:5-diethyltetrahydrofuran, b. p. 192°,  $D^{25}_D$  0.9317,  $n_D$  1.4368, forms a semicarbazone, m. p. 136—138°. 3-Keto-2:5-diisobutyltetrahydrofuran, b. p. 112—114°/15 mm.,  $D^{24}_D$  0.9066,  $n_D$  1.4385. 3-Keto-2:2:5:5-tetraethyltetrahydrofuran, b. p. 110°/18 mm.,  $D^{24}_D$  0.9275,  $n_D$  1.4486. 3-Keto-2:5-dipentamethylene-tetrahydrofuran,  $C_8H_6 \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \text{C} \begin{smallmatrix} \text{CO} \cdot \text{CH}_2 \\ \text{O} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} C_3H_6$ , has b. p. 152—154°/18 mm.,  $D^{24}_D$  1.0268,  $n_D$  1.4904; the semicarbazone has m. p. 216°. W. O. W.

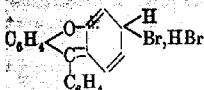
Condensation of *p*-Dibromobenzene with Xanthone; Quinocarbonium Salts. LEE H. CONE and C. J. WEST (*J. Amer. Chem. Soc.*, 1911, 33, 1538—1548).—By the action of xanthone on the products resulting from dibromobenzene and magnesium, *p*-phenylenedixanthanol,  $(O \begin{smallmatrix} \text{C}_6H_4 \\ \text{C}_6H_4 \end{smallmatrix} \text{C} \cdot OH)_2 C_6H_4$ , is formed in addition to *p*-bromophenylxanthanol (Gomberg and Cone, Abstr., 1909, i, 55; 1910, i, 869). This is the simplest member of a new series of xanthenols with two reactive nuclei; with hydrochloric acid a coloured diacid chloride and a colourless normal dichloride are formed. The influence of the bridge oxygen is brought to light by a comparison with tetraphenyl-*p*-xylylene glycol,  $OH \cdot CPh_2 \cdot C_6H_4 \cdot CPh_2 \cdot OH$  (Thiele and Balhorn, Abstr., 1904, i, 491).

This glycol gives with hydrogen bromide in acetic acid solution a colourless bromide, which with metallic silver or copper yields a quinonoid orange-coloured hydrocarbon, tetraphenyl-*p*-xylylene, which is not at all an analogue of triphenylmethyl.

*p*-Phenylenedixanthanol gives with hydrogen chloride a coloured dihydrochloride, from which a colourless simple chloride can be prepared. Silver removes the chlorine from this chloride, forming an unsaturated hydrocarbon, which is a true isologue of triphenylmethyl. A colourless bromide could not be obtained.

*p*-Phenylenedixanthanol forms colourless crystals, m. p. 176—177°. The chloride-hydrochloride is a bright red, crystalline powder; on heating a suspension in benzene, hydrogen chloride is evolved and a clear, colourless solution of the chloride,  $C_6H_4(CCl \begin{smallmatrix} \text{C}_6H_4 \\ \text{C}_6H_4 \end{smallmatrix} O)_2$ , remains. This darkens at 210°, m. p. 259—260°. It forms a number of salts characterised by their great insolubility and high melting points. The ferrichloride forms orange-red crystals; the zincichloride is somewhat darker in colour; the stannichloride separates in finely divided orange crystals; the mercurichloride gives dull red crystals; the perbromide forms yellow crystals; the periodide is a dark brown, nearly black, powder; the perchlorate separates in fine reddish-yellow crystals, and the hydrogène sulphate is a crystalline powder.

*p*-Phenylenediquinoxanthanol bromide hydrobromide (annexed formula)

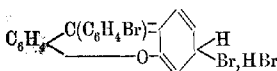


is obtained in reddish-brown crystals; the bromide is a red solid, and has not been obtained in a colourless form.

The following salts of *p*-bromophenylxanthanol are described: *ferrichloride*, orange-yellow needles, m. p. 218°; *zincchloride* double salt, large, shimmering, dark orange plates, m. p. 235°; *stannichloride*, dark yellow crystals, m. p. 185°; *mercurichloride*, light orange-yellow crystals,

which turn bright yellow at 160°, soften at 250°, m. p. 257° to a dark liquid. The *perbromide* of the *chloride* forms fine glistening, light orange needles, m. p. 201—202°; the *periodide* appears in dark purple, shining needles, m. p. 188°. The *hydrogen sulphate* crystallises in large plates, which are brown in transmitted light, and have a green metallic lustre in reflected light, m. p. 77—78°.

*p*-Bromophenylquinoxanthanol bromide hydrobromide (annexed formula), prepared by the addition of acetyl bromide to a solution of the



xanthanol, forms very hygroscopic, dark orange-red crystals. It loses hydrogen bromide, forming *p*-bromophenylxanthanol bromide,

$C_{19}H_{12}OBr_3$ , which is colourless.

The *zincbromide* separates in bright red crystals, m. p. 250° to a dark red liquid; the *mercuribromide* yields yellow crystals, m. p. 247—248° to a dark red liquid. The *bromide perbromide* is obtained as orange crystals, m. p. 188°; the *bromide periodide* forms deep purple, lustrous crystals, m. p. 211—212° to a dark purple liquid.

E. F. A.

5-Methylthiophen-2-aldehyde. E. GRISHKEWITSCH-TROCHIMOWSKY (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 803—806. Compare this vol., i, 481).—In ethereal solution, 2-iodo-5-methylthiophen readily reacts with magnesium, forming the corresponding iodo-magnesium derivative, which, when treated with ethyl orthoformate,

yields the *acetal*,  $\begin{matrix} \text{CMe-S} \\ | \\ \text{CH-CH} \end{matrix} > \text{C-CH(OEt)}_2$ , as a colourless, viscous liquid with a pleasant fruity odour, b. p. 236.5—238°/747 mm.,  $D_4^{20}$  1.0388,  $n_D^{20}$  1.48953.

5-Methylthiophen-2-aldehyde,  $\begin{matrix} \text{CH=CMe} \\ | \\ \text{CH-C(CHO)} \end{matrix} > \text{S}$ , obtained by hydrolysing the acetal with hydrochloric acid in a current of carbon dioxide, is a colourless, refractive liquid with an odour of bitter almonds, b. p. 218—219.5°/749 mm.,  $D_4^{21}$  1.1698,  $n_D^{21}$  1.58166. Its *phenylhydrazone*,  $C_{12}H_{13}N_2S$ , forms faintly yellow needles, m. p. 116—117°.

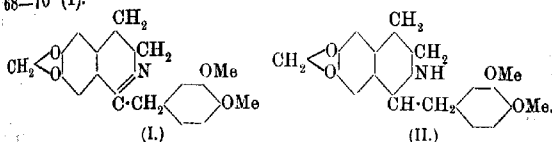
An ethereal solution of the aldehyde saturated with ammonia in the cold gradually deposits the *hydramide*,  $(C_4H_5SMe \cdot CH)_2N_2$ , in rosettes of colourless needles, m. p. 124.5—125.5°; the hydramide is decomposed into its components when gently heated with dilute mineral acid.

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The action of carbon dioxide on the above iodo-magnesium complex gives 5-methylthiophen-2-carboxylic acid in almost quantitative yield.

T. H. P.

**Synthesis of Berberine.** AMÉ PICTET and ALPHONSE GAMS (*Compt. rend.*, 1911, 153, 386—388; *Ber.*, 1911, 44, 2480—2485. Compare this vol., i, 483).—The complete synthesis of berberine has now been accomplished in the following steps. Homopiperonylamine condenses with homoveratroyl chloride to give homoveratroylhomopiperonylamine,  $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_4\text{:CH}_2\text{:CH}_2\text{:NH}\cdot\text{CO}\cdot\text{CH}_2\text{:C}_6\text{H}_4\text{:OMe}$ , long needles, m. p. 136°. This loses  $1\text{H}_2\text{O}$  when boiled with phosphoric oxide in xylene solution, and forms the unsaturated compound, m. p. 68—70° (I).



Reduction of this tertiary base with tin and hydrochloric acid leads to the formation of veratrylnorhydrohydrastinine, slender needles, m. p. 208—210° (II). A methylene group is introduced between the imino-group and the veratryl ring by condensing the product with methylal in presence of hydrochloric acid. The tetrahydroberberine so obtained is identical with that prepared by Perkin from natural berberine, and yields this substance when treated with oxidising agents.

W. O. W.

**The Alkaloids of the Toadstool and "Artificial" Muscarine.** J. HONDA (*Arch. exp. Path. Pharm.*, 1911, 65, 454—466).—A method is described by which muscarine can be obtained from toadstools and freed from the choline also invariably present. In addition to these two substances, two other alkaloids were also isolated, and named  $\alpha$ - and  $\beta$ -myketosine. The quantities obtained were too small for analysis.

The muscarine thus isolated has the same physiological action as "artificial" muscarine obtained by the oxidation of choline platinichloride.

E. J. R.

**Cyclic Ammonium Bases.** HERMAN DECKER and ADOLF KAUFMANN (*J. pr. Chem.*, 1911, [ii], 84, 219—246).—The first part of this paper is mainly a review of previous work on the constitution of the  $\psi$ -ammonium bases. This is followed by a discussion of the subjects enumerated below.

(I) *Constitution of the Carbinol Bases.*—The author criticises the view that the  $\psi$ -ammonium bases have an aldehydic or ketonic structure. The formation of anhydrides of the carbinol bases observed by Kaufmann and Strübin (this vol., i, 321) furnishes no evidence in support of the aldehydic structure. Reference is made to the formation of symmetrical ethers of carbinol bases of other classes,

and the preparation of the *anhydride* of 2-hydroxy-9-phenylxanthen-9-ol,  $(C_{19}H_{11}O_2)_2O$ , m. p.  $246^\circ$ , is described.

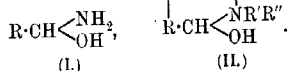
(II) *Constitution of the Cyanines*.—In this section the author discusses the constitution of the cyanine dyes, and explains the mechanism of the reactions by which they are formed.

(III) *The Negative Properties of the Nitrogen Atom in Aromatic Rings*.—The substitution processes occurring in heterocyclic rings are readily explicable on the assumption that the nitrogen atom exercises an orientating influence, similar to that of a strongly negative group, such as the nitro-group. The mobility of the atoms or groups in the 2- or 4-position of the pyridine ring is referred by the author to the same negative property of the nitrogen atom.

(IV) *Constitution of the apocyanines*.—The negative influence referred to in the preceding section is the factor which determines the formation of the apocyanines. Owing to this negative property of the nitrogen atom, the hydrogen occupying the 2-position in the quinoline molecule is very reactive, and condensation, therefore, readily takes place in this position. Kaufmann and Strübin's (this vol., i, 328) assumption that 1:2-dihydroquinoline is an intermediate product in the formation of the apocyanine dyes thus becomes unnecessary.

(V) *The Aldehydic Function of Carbinol Bases*.—In this section attention is drawn to the great similarity in the reactions of aldehydes and carbinol bases, and to the remarkable activity of the hydroxyl group.

(VI) *The Cause of the Aldehydic Function of Carbinol Bases*.—A comparison of the formulae of the aldehyde-ammonias (I) and the  $\psi$ -ammonium bases (II) at once reveals the fact that these compounds are similarly constituted:



It is to this similarity of structure that the remarkable resemblance in the reactions of aldehydes and  $\psi$ -ammonium bases is due. F. B.

**The Splitting of the Pyrrolidine Ring by Bacteria**  
DANKWART ACKERMANN (*Zeitsch. Biol.*, 1911, 57, 104—111).—*dl*-Proline, obtained by the hydrolysis of gelatin with baryta according to Fischer and Bochner's method, was acted on by a mixed culture of putrefaction bacteria in a culture solution containing Witte's peptone and dextrose. The solution was kept slightly alkaline. If the decomposition proceeded in the manner usual for amino-acids, pyrrolidine should be formed, but this substance could not be detected; instead, the ring was broken and  $\delta$ -aminovaleric acid was formed by the addition of two atoms of hydrogen. Arginine is also decomposed by bacteria with formation of the same acid. E. J. R.

**The Reactivity of the  $\beta$ -Unsubstituted Pyrrole Ring**  
W. KÖNIG (*J. pr. Chem.*, 1911, [ii], 84, 194—219).—The reactions of  $\beta$ -unsubstituted indole and pyrrole derivatives are compared with those of primary amines and of compounds containing a reactive

methylene group. It is shown that there is a remarkable resemblance in the chemical behaviour of these three groups.

Guided by this similarity, the author attempted to prepare 2-methylindole-3-aldoxime by heating a methyl-alcoholic solution of 2-methylindole with mercury fulminate and hydrochloric acid, but obtained, instead of the aldoxime, the mercurichloride of a red dye, which proved to be identical with that prepared by Ellinger and Flamand (this vol., i, 329) from 2-methylindole-3-aldehyde and dilute sulphuric acid. From the analysis of numerous salts, and from quantitative experiments on the formation of the perchlorate and mercurichloride, as well as from many other considerations, the author conclusively proves that the dye base has the composition  $C_{19}H_{16}N_2$ , and not  $C_{18}H_{15}N_2$ , as stated by Ellinger and Flamand. When heated with phenylhydrazine, it yields 2-methylindole and 2-methylindole-3-aldehydophenylhydrazone,  $NH \langle \begin{smallmatrix} C_6H_4 \\ CM_6 \end{smallmatrix} \rangle C \cdot CH : N \cdot NHPh$ , which crystal-

lises in lustrous, colourless needles, m. p.  $201^\circ$ . Both this reaction and the similar decomposition by hydrolysis into 2-methylindole and 2-methylindole-3-aldehyde are in agreement with the formula,  $NH \langle \begin{smallmatrix} C_6H_4 \\ CM_6 \end{smallmatrix} \rangle C \cdot CH : C \langle \begin{smallmatrix} C_6H_4 \\ CM_6 \end{smallmatrix} \rangle N$ , proposed by the author.

The dyes are therefore derivatives of 3-indyl-3-indolidenemethane, and not of tri-indylmethane, as supposed by Ellinger and Flamand.

The mercurichloride,  $C_{19}H_{17}N_2Cl, HgCl_2$ , crystallises with one molecule of methyl alcohol in large, apparently rhombic plates with a green lustre, m. p.  $197^\circ$ ; these lose their methyl alcohol at  $120^\circ$ , and are transformed into red needles having a violet lustre. The mercuribromide, prepared from 2-methylindole, mercury fulminate, and hydrobromic acid, forms brownish-red crystals, also containing one molecule of methyl alcohol, m. p.  $193^\circ$ .

Similar mercurihalides have been obtained from 2:5-dimethylindole and 2-phenyl-5-methylpyrrole.

2-Methylindole-3-aldoxime,  $C_{16}H_{15}ON$ , prepared by heating the aldehyde with hydroxylamine hydrochloride and pyridine, crystallises in long, colourless needles, m. p.  $154^\circ$ . When boiled with acids, it is slowly converted into the above-mentioned dye; the transformation takes place much more readily in the presence of mercuric chloride.

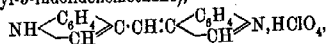
The salts of the dye are best prepared by the addition of a slight excess of the requisite acid to 2-methylindole-3-aldehyde dissolved in six to eight times its weight of alcohol. The hydrochloride,

$C_{19}H_{16}N_2, HCl$ , m. p.  $248^\circ$ ; the hydrobromide, m. p.  $218^\circ$ ; the hydriodide, m. p.  $228-230^\circ$ , and the perchlorate,  $C_{19}H_{16}N_2, HClO_4$ , m. p.  $248^\circ$  (decomp.), all crystallise in red or brownish-red needles containing one molecule of methyl alcohol; the sulphate, m. p.  $215^\circ$  with previous sintering, has the composition  $C_{19}H_{16}N_2, H_2SO_4$  (compare Ellinger and Flamand, *loc. cit.*).

A general method for the preparation of the dyes of the 3-indyl-3-indolidenemethane series is described. Ethyl orthoformate (1 mol.) and indole or its derivatives (2 mols.) are dissolved in the smallest possible quantity of alcohol and treated with the calculated amount



of the acid, the salt of which is required. The following compounds were prepared in this manner: the *perchlorate* of the dye from indole (3-indyl-3-indolidenemethane),



crystallising in ruby-red needles with a green lustre, m. p. 276°; the corresponding sulphate (compare Ellinger and Flamand, *Abstr.*, 1909, i, 846), and the *perchlorate*,  $\text{C}_{21}\text{H}_{20}\text{N}_2 \cdot \text{HClO}_4$ , from 2:5-dimethylindole; the latter compound crystallises with one molecule of alcohol in long, bright red needles, which lose their alcohol at 120°, and have m. p. 245°.

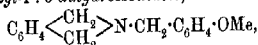
Similar salts have been prepared from 1-alkylindoles, 2-phenyl-5-methylpyrrole, and 3-methylindole.

The dyes of this series are also obtained in small yield by the action of hydrocyanic acid and hydrogen chloride on indole and its derivatives in the presence of aluminium chloride. F. B.

*p*-Hydroxybenzylamine. MARC TIFFENEAU (*Bull. Soc. chim.*, 1911, [iv], 9, 819—824. Compare this vol., i, 778).—The author has undertaken the investigation of this phenolic base and of certain of its homologues in view of their close connexion with hordenine, and analogous substances, of marked physiological activity (compare Barger, *Trans.*, 1909, 95, 1123, 2193, and Barger and Walpole, *ibid.*, p. 1720).

*p*-Hydroxybenzylamine, prepared from anisylamine by the action of hydriodic acid, was used in the form of the *hydrochloride*, m. p. 195°; the *hydriodide* melts at 198—200°.

2-*p*-Methoxybenzyl-1:3-dihydroisindole,



m. p. 83°, obtained by von Braun's method (*Abstr.*, 1910, i, 506) from *o*-xylylene bromide and anisylamine, crystallises in needles, and is very soluble in alcohol; the *hydrobromide*, m. p. 234°, crystallises in spangles, and the *methiodide* has m. p. 183°. When boiled with acetic anhydride,

anisyl acetate and 2-acetyl-1:3-dihydroisindole,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \text{N} \cdot \text{Ac}$ ,

m. p. 77°, b. p. 180—200°/15 mm., are formed. The latter crystallises in needles from boiling light petroleum. T. A. H.

**Hydrazones.** ROBERTO CIUSA and L. VECCHIOTTI (*Atti R. Acad. Lincei*, 1911, [v], 20, i, 803—807. Compare *Abstr.*, 1910, i, 196).—The *p*-nitrophenylhydrazones of benzaldehyde, and *o*-, *m*-, and *p*-nitrobenzaldehyde exhibit chromoisomerism similar to that previously discussed. The *p*-nitrophenylhydrazone of anisaldehyde, however, was not obtained in two modifications. Benzaldehyde-*p*-nitrophenylhydrazone (compare Hyde, *Abstr.*, 1899, i, 688) when recrystallised from alcohol forms orange needles, m. p. 195—196°. When precipitated from warm alcohol with water, it is transformed into yellow scales, m. p. 195°. If, however, the precipitation is effected in the cold, a red form is obtained in needles or scales, which become yellow at 140° and melt at 194°. The yellow variety can be transformed into

the other by recrystallisation from formamide, from which solvent only the red form is deposited. The red and yellow modifications thus appear to be distinct, whilst the orange-coloured products, which can be prepared by the action of various solvents, represent one or more mixtures, combinations, or solid solutions of these two.

*o*-Nitrobenzaldehyde-*p*-nitrophenylhydrazone when recrystallised from glacial acetic acid forms orange-red needles, which become red at 190°, and melt at 250–251°. By precipitation with water from alcohol, it is converted into an orange-yellow modification, m. p. 250–251°.

*m*-Nitrobenzaldehyde-*p*-nitrophenylhydrazone (Hyde, *loc. cit.*) crystallises from acetic acid in orange-red crystals, m. p. 250–251°, which, by precipitation with water from alcohol, are converted into the yellow form, m. p. 248°. This form when heated to 130° acquires an increasing red tint, but regains its original colour on cooling (thermochromism).

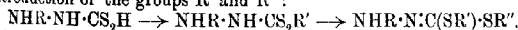
*p*-Nitrobenzaldehyde-*p*-nitrophenylhydrazone (Hyde, *loc. cit.*) crystallises from glacial acetic acid in brick-red scales, m. p. 247°. From alcohol an orange-yellow form, m. p. 245°, is obtained.

*Anisaldehyde-p-nitrophenylhydrazone* forms small, reddish-violet needles, m. p. 160°; only one modification could be isolated, but the addition of water to its solution in acetone gives a yellow precipitate which becomes red immediately. R. V. S.

**Isomeric Hydrazones of Dithiocarbonic Esters.** MAX BUSCH and HERMANN KRAFF (*J. pr. Chem.*, 1911, [ii], 84, 293–304).—It has been shown previously (Abstr., 1901, i, 430) that the phenylhydrazones of unsymmetrical esters of dithiocarbonic acid exist in two stereoisomeric forms,  $\begin{array}{c} \text{RS}\cdot\text{C}\cdot\text{SR}' \\ | \\ \text{N}\cdot\text{NHPh} \end{array}$  and  $\begin{array}{c} \text{RS}\cdot\text{C}\cdot\text{SR}' \\ | \\ \text{NHPh}\cdot\text{N} \end{array}$ , which appear

to be equally stable. In extending the investigation to the *p*-tolylhydrazones and *p*-bromophenylhydrazones, the authors have met with a marked difference in the stability of the isomerides. Thus, of the isomeric *p*-tolylhydrazones of methyl *p*-nitrobenzyl dithiocarbonate, the more fusible modification is the less stable form, and is completely transformed at 100° into the less fusible, stable isomeride.

The isomeric hydrazones described below were prepared by successively introducing two different groups into *p*-tolylidithiocarbazine acid or *p*-bromophenyldithiocarbazine acid by the action of alkyl or aryl halides on the potassium salts of the acids, or of their esters in aqueous alcoholic solution, at the ordinary temperature, the different modifications being produced by varying the order of introduction of the groups R' and R'':

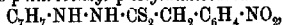


The isomerides are distinguished by naming the two groups in the order in which they are introduced. It is assumed that the group first introduced and the hydrazine residue occupy the *anti*-positions.

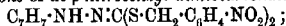
The phenylhydrazone of benzyl *o*-nitrobenzyl dithiocarbonate,  $\text{C}_6\text{H}_5\cdot\text{S}\cdot\text{C}(\text{S}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2):\text{N}\cdot\text{NHPh}$ , prepared from *o*-nitrobenzyl chloride and benzyl phenyldithiocarbazine, crystallises in clusters of red needles, m. p. 67°. The isomeric *o*-nitrobenzyl benzyl dithiothio-

carbonate phenylhydrazones, prepared from benzyl chloride and *o*-nitrobenzyl phenyldithiocarbazine, forms lustrous, light red columns, m. p. 88°. Both forms have the same solubility, and, when heated separately at 100°, are converted into a mixture consisting of the two isomerides in equal proportions.

The interaction of *p*-nitrobenzyl chloride and potassium *p*-tolylthiocarbazine yields *p*-nitrobenzyl *p*-tolylthiocarbazine,



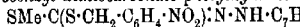
which crystallises in stout, yellow needles, m. p. 127°, together with the *p*-tolylhydrazone of *di-p*-nitrobenzyl dithiocarbonate,



the latter compound forms lustrous, red, pointed needles, m. p. 116°.

*o*-Nitrobenzyl *p*-tolylthiocarbonate, prepared in a similar manner to the preceding *p*-nitro-compound, crystallises in yellow needles, m. p. 147°, which become green when kept. It is accompanied by *di-o*-nitrobenzyl dithiocarbonate *p*-tolylhydrazone, crystallising in very slender, felted, golden-yellow needles, m. p. 134°.

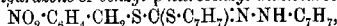
Methyl *p*-nitrobenzyl dithiocarbonate *p*-tolylhydrazone,



prepared from methyl *p*-tolylthiocarbazine and *p*-nitrobenzyl chloride, forms lustrous, garnet-red, pointed needles, m. p. 115°; the isomeric *p*-nitrobenzyl methyl dithiocarbonate *p*-tolylhydrazone, prepared by methylating *p*-nitrobenzyl *p*-tolylthiocarbazine, crystallises in tufts of glassy, golden-yellow needles, m. p. 57°. The former isomeride is the stable form, and remains unchanged when heated above its m. p.

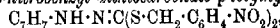
Ethyl *p*-nitrobenzyl dithiocarbonate *p*-tolylhydrazone,  $\text{C}_{17}\text{H}_{19}\text{O}_2\text{N}_2\text{S}_2$ , crystallises in lustrous, red leaflets, m. p. 70°; the isomeride is a red oil.

The *p*-tolylhydrazone of benzyl *p*-nitrobenzyl dithiocarbonate,



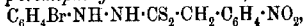
prepared from *p*-nitrobenzyl chloride and benzyl *p*-tolylthiocarbazine, is identical with the hydrazone obtained by the interaction of benzyl chloride and *p*-nitrobenzyl *p*-tolylthiocarbazine; it crystallises in tufts of red needles or garnet-red, quadrilateral plates, m. p. 119°.

*o*-Nitrobenzyl *p*-nitrobenzyl dithiocarbonate *p*-tolylhydrazone,



forms slender, orange needles, m. p. 124°; the isomeride, light red columns, m. p. 80°.

*p*-Nitrobenzyl *p*-bromophenyldithiocarbazine,



crystallises in long, transparent, light yellow needles, m. p. 135–136°; it is obtained together with the *p*-bromophenyldiazones of *di-p*-nitrobenzyl dithiocarbonate,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{N}:\text{C}(\text{S}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$ , which forms lustrous, red needles, m. p. 132°, by the interaction of *p*-nitrobenzyl chloride and potassium *p*-bromophenyldithiocarbazine.

*o*-Nitrobenzyl *p*-bromophenyldithiocarbazine, prepared in a similar manner, crystallises in slender, white needles, m. p. 156–157°; the accompanying *di-o*-nitrobenzyl dithiocarbonate *p*-bromophenyldiazones, felted, light red needles, m. p. 119°.

The *p*-bromophenylhydrazones or methyl *p*-nitrobenzyl dithiocarbonate,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{S}\cdot\text{C}(\text{SMe})\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{Br}$ , could only be obtained in one form; it crystallises in slender, monoclinic prisms, capped with dimorphs or pyramids, and has m. p.  $119^\circ$  or  $120$ — $121^\circ$ , according to the method of preparation.

*o*-Nitrobenzyl *p*-nitrobenzyl dithiocarbonate *p*-bromophenylhydrazones,  $\text{C}_{12}\text{H}_{10}\text{O}_4\text{N}_4\text{BrS}_2$ , crystallises in clusters of small, stout, golden-yellow needles, m. p.  $113$ — $114^\circ$ ; the isomeride forms felted, orange-red needles, m. p.  $107^\circ$ . When fused for some time, each modification yields a mixture of the two isomerides in approximately equal proportions.

The benzoylphenylhydrazones of methyl ethyl dithiocarbonate,  $\text{SMe}\cdot\text{C}(\text{SEt})\cdot\text{N}\cdot\text{NPhBz}$ , prepared from methyl benzoylphenyldithiocarbazine and ethyl iodide, crystallises from alcohol in colourless, transparent columns, m. p.  $93^\circ$ , and from light petroleum in pointed needles, m. p.  $94^\circ$ . The isomeric ethyl methyl dithiocarbonate benzoylphenylhydrazones, obtained from ethyl benzoylphenyldithiocarbazine and methyl iodide, separates from alcohol in stout, white needles, m. p.  $83$ — $84^\circ$ , and from light petroleum in hard needles of a diamond lustre, m. p.  $85$ — $86^\circ$ .

F. B.

Hydantoins. IV. Reduction of Aldehyde Condensation Products of 2-Thio-1-phenylhydantoin. TREAT B. JOHNSON and CHARLES A. BRAUTLECHT (*J. Amer. Chem. Soc.*, 1911, 33, 1531—1538). —Wheeler and Hoffmann (this vol., i, 498) have shown that on condensation of hydantoin with aldehydes, unsaturated compounds are formed, which when warmed with hydriodic acid are reduced at the double bond and transformed quantitatively into alkyl-hydantoins. These are hydrolysed by acids or alkalis to the corresponding amino-acids.

2-Thio-1-phenylhydantoin likewise condenses with aldehydes, but its derivatives are not reduced at the double bond by hydriodic acid. Zinc dust and acetic acid, or ammoniacal ferrous sulphate, were also ineffective, but sodium amalgam effected a quantitative transformation into the alkylthiohydantoins. These compounds could not be hydrolysed by sodium or barium hydroxides to  $\alpha$ -amino-acids.

2-Thio-1-phenyl-4-benzylidenehydantoin is attacked by chlorine and bromine in glacial acetic acid solution. 2-Thio-1-phenyl-4-*chloro*-benzylidenehydantoin,  $\text{NPh}\begin{matrix} \text{CO}\cdot\text{C}\cdot\text{CClPh} \\ \text{CS}\cdot\text{NH} \end{matrix}$ , crystallises in colourless

prisms, m. p.  $236$ — $237^\circ$ . The corresponding *o*-bromobenzylidene compound separates in yellow plates, m. p.  $211^\circ$ .

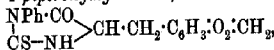
On reduction of 2-thio-1-phenyl-4-benzylidenehydantoin with sodium amalgam, the same 2-thio-1-phenyl-4-benzylhydantoin is obtained as is obtained by the interaction of phenylthiocarbamide and phenylalanine (Brautlecht).

On alkylation of this with ethyl bromide in presence of sodium hydroxide, 2-ethylthio-1-phenyl-4-benzylhydantoin is formed as an oil, which when digested with hydrochloric acid is converted into 1-phenyl-benzylhydantoin.

2-Thio-1-phenylhydantoin-4-glyoxylic acid,  $\begin{array}{c} \text{NPh}\cdot\text{CO} \\ | \\ \text{CS}-\text{NH} \end{array} > \text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , prepared by the interaction of ethyl oxalate and 2-thio-1-phenylhydantoin, crystallises in pale yellow needles, m. p. 240° (decomp.).

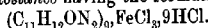
2-Thio-1-phenyl-4-p-methoxybenzylhydantoin crystallises in slender, colourless prisms, m. p. 171°.

2-Thio-1-phenyl-4-piperonylhydantoin,



is obtained in straw-coloured needles, m. p. 172—173°. E. F. A.

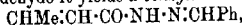
Compound of Antipyrine with Ferric Chloride, obtained with Ferrous Chloride. CHARLES ASTRE and J. VIDAL (*Bull. Soc. chim.*, 1911, [iv], 9, 836—839. Compare this vol., i, 399).—A solution of ferrous chloride to which antipyrine dissolved in hydrochloric acid has been added develops a gooseberry-red coloration, and on evaporation and treatment of the syrupy residue with ether, deposits yellowish-green crystals of a substance having the formula



This becomes pasty at 121—122°, and dissolves in water, forming a gooseberry-red solution, which becomes yellowish-green on addition of an acid, or enough alkali to neutralise it. The solution gives the usual reactions of ferric iron, antipyrine, and chlorides. The ferric iron is reduced to the ferrous state by sodium nitrite, hydrogen sulphide, or sulphur dioxide, but not by zinc and acetic acid. The compound is quite distinct from that with ferric chloride, called ferripyrine, described by Schuyten (*Abstr.*, 1896, i, 575).

T. A. H.

Formation of 1-Nitroso-5-methyl-3-pyrazolidone from Crotonoylhydrazide. ERNST MUCKERMANN (*J. pr. Chem.*, 1911, [ii] 84, 278—292. Compare this vol., i, 682).—Crotonoylhydrazide,  $\text{CHMe}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ , is obtained as a viscid liquid by the interaction of ethyl crotonate and hydrazine hydrate in alcoholic solution. It possesses the usual reducing properties, and forms a hydrochloride, crystallising in snow-white needles, m. p. 173° (decomp.). When treated with benzaldehyde it yields a benzylidene derivative,



m. p. 72°; the *o*-hydroxybenzylidene derivative,  $\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_2$ , has m. p. 190°; the *p*-methoxybenzylidene derivative,  $\text{C}_{12}\text{H}_{14}\text{O}_2\text{N}_2$ , crystallises in yellowish-white needles, m. p. 99°.

Crotonylsemicarbazide,  $\text{CHMe}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , prepared by the interaction of crotonoylhydrazide hydrochloride and potassium cyanate in aqueous solution, crystallises in stout prisms, m. p. 171°.

When treated with sodium nitrite, the hydrazide hydrochloride is converted into 1-nitroso-5-methyl-3-pyrazolidone. This crystallises in lustrous, white leaflets, m. p. 131°, and gives a cherry-red coloration with ferric chloride; the ammonium salt,  $\text{C}_4\text{H}_{10}\text{O}_2\text{N}_4\cdot\frac{1}{2}\text{H}_2\text{O}$ , forms radiating needles, m. p. 144° (decomp.); the silver salt,  $\text{C}_4\text{H}_6\text{O}_2\text{N}_4\cdot\text{Ag}$ , forms lustrous, silky needles, m. p. 148—149° (decomp.); the copper salt,  $\text{Cu}(\text{C}_4\text{H}_6\text{O}_2\text{N}_2)_2\cdot 2\text{H}_2\text{O}$ , stout, dark blue, monoclinic prism

$a:b:c = 1.29:1:0.85$ ;  $\beta = 101^\circ 30'$  (Beder). The ammonium salt forms with picric acid a compound,  $C_6H_{10}O_2N_4 \cdot C_6H_3O_7N_3$ , which crystallises with one molecule of ethyl alcohol in lustrous, golden-yellow, monoclinic columns, m. p. 162–164°.

1-Nitroso-5-methyl-2-ethyl-3-pyrazolidone,  $C_8H_{11}O_2N_2$ , obtained by the action of ethyl iodide on the above-mentioned silver salt, separates from ether in colourless, monoclinic plates, m. p. 83°.

When 1-nitroso-5-methyl-3-pyrazolidone is treated with bromine in glacial acetic acid solution below 10°, it yields 4-bromo-3-methyl-5-pyrazolone,  $C_6H_8ON_2Br$ , which crystallises in colourless, hexagonal platelets, m. p. 182°, and may also be obtained by brominating 3-methylpyrazolone (Curtius and Jay, Abstr., 1889, 393). The interaction of 1-nitroso-5-methyl-3-pyrazolidone and excess of bromine in glacial acetic acid solution yields 4:4-dibromo-3-methyl-5-pyrazolone,  $C_6H_6ON_2Br_2$ . This crystallises in short, monoclinic columns, m. p. 132°, and may also be prepared by brominating 3-methylpyrazolone (compare Rothenburg, Abstr., 1895, i, 686). The compound described by Rothenburg as 4:4-dibromo-3-methylpyrazolone of m. p. 182° is probably identical with the above-mentioned 4-bromo-3-methylpyrazolone.

F. B.

**Hydroxyindazoles. V. Constitution.** PAUL FREUNDLER (*Bull. Soc. chim.*, 1911, [iv], 9, 778–784. Compare this vol., i, 577, 753). Further proof is given of the constitution of the chlorinated hydroxyindazoles obtained from substituted benzeneazo-*o*-benzoic acids. The presence of an indazole nucleus is shown by the fact that 5:7-dichloro-3-hydroxy-2-phenylindazole yields, on treatment with phosphorus pentachloride in the presence of phosphoryl chloride, 3:5:7-trichloro-2-phenylindazole, needles, m. p. 172.5°. This substance can also be obtained by direct chlorination of 2-phenylindazole of known constitution.

The position of the hydroxyl group is shown in that on oxidation of the hydroxyindazole by moderate oxidising agents it is transformed into 2-benzeneazo-3:5-dichlorobenzoic acid,  $N_2Ph \cdot C_6H_2Cl_2 \cdot CO_2H$ , red prisms, m. p. 142.5–143°, which is also obtained by the oxidation of the above-mentioned trichloro-compound. On reduction, it yields aniline and 3:5-dichloroanthranilic acid, thus proving the position of the chlorine atoms.

Further, the hydroxyindazole yields a benzoyl derivative, long needles, m. p. 203.5–204°, and a methyl ether, tabular prisms, m. p. 44–144.5°.

W. G.

**Crystallographical Examination of Inactive Ornithine monopicrate.** P. REINER (*Zeitsch. physiol. Chem.*, 1911, 73, 92–193).—The triclinic crystals of *dl*-ornithine monopicrate, m. p. 70° (compare Kossel and Weiss, Abstr., 1910, ii, 909), have  $a:b:c = 0.6962:1:0.6301$ ;  $\alpha = 93^\circ 10'$ ,  $\beta = 100^\circ 55'$ ,  $\gamma = 81^\circ 19'$ .

E. F. A.

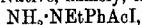
**Extractives of Muscles. XII. Constitution of Carnosine.** VLADIMIR VON GULEWITSCH (*Zeitsch. physiol. Chem.*, 1911, 73, 34–446. Compare Skwarzoff, Abstr., 1910, ii, 879).—The author

has suggested (Abstr., 1907, i, 337) that the products of hydrolysis of carnosine by barium hydroxide are histidine and a substance  $C_3H_5O_2N$ , probably alanine.

It is now established that three-quarters of the carnosine-nitrogen belong to histidine and the rest to a substance which is not *DL*- $\alpha$ -alanine, but is proved to be  $\beta$ -alanine, m. p. 230—232°. Carnosine is accordingly  $\beta$ -alanylhistidine or histidyl- $\beta$ -alanine, and may have been derived from asparagylhistidine or histidyl-lysine by the loss of an amino-group and elimination of a carbon atom, so that the  $\beta$ -alanyl residue is formed.

E. F. A.

*N*-Amino-heterocyclic Compounds. III. Properties of  $\alpha$ -Acylhydrazines, 1-Amino-2:5-diphenyl-1:3:4-triazole, and 1-Amino-2:5-dibenzyl-1:3:4-triazole. HARTWIG FRANZEN and F. KRAFT (*J. pr. Chem.*, 1911, [ii], 84, 122—139. Compare FRANZEN and Scheuermann, Abstr., 1908, i, 293).—The reactions previously described (*loc. cit.*) as characteristic of *as. sec.*-hydrazines are also given by  $\alpha$ -acylhydrazines, with the exception of the reaction with pyruvic acid. When  $\alpha$ -acetyl- or  $\alpha$ -benzoyl-phenylhydrazine is boiled with alcohol and precipitated mercuric oxide, the latter rapidly turns black, and dark-coloured oily products are obtained when the alcoholic solutions are evaporated. It has not been settled whether tetrazones are formed as intermediate products.  $\alpha$ -Acetylphenylhydrazine forms a quaternary nitrogen derivative, namely, the *ethiodide*,



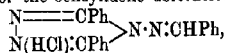
when heated with ethyl iodide at 100° for several hours; this crystallises from alcohol, and has m. p. 201°.  $\alpha$ -Benzoylphenylhydrazine under similar conditions gives tarry products.

1-Amino-2:5-diphenyl-1:3:4-triazole (Pinner, Abstr., 1894, i, 386) and 1-amino-2:5-dibenzyl-1:3:4-triazole (Pinner, Abstr., 1897, i, 640) have been examined as further examples of *N*-amino-heterocyclic compounds. Their behaviour resembles that of similar compounds already studied (Abstr., 1906, i, 706; 1908, *loc. cit.*). They are not affected when boiled with alcohol and mercuric oxide, and do not condense with acetophenone, acetone, or pyruvic acid. The diphenyl derivative reacts slowly with aldehydes, for example, with benzaldehyde, it yields the benzylidene derivative,  $C_6H_5N_3 \cdot N:CHPh$ , which forms salts with most acids.

Tertiary hydrazines can be obtained by reducing the condensation products of aromatic aldehydes and alcohol with *as. sec.*-hydrazines by means of sodium amalgam; phenylbenzylbenzylidenehydrazine yields  $\alpha$ -phenyl- $\alpha$ - $\beta$ -dibenzylhydrazine, and dibenzylbenzylidenehydrazine yields tribenzylhydrazine. The condensation products of 1-amino-2:5:4-phenyltriazole with aldehydes can be reduced in a similar manner.

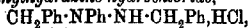
The best yields of 1-amino-2:5-diphenyl-1:3:4-triazole are obtained by the action of an alcoholic solution of hydrogen chloride on diphenyldihydro-tetrazine. Its *picrate*,  $C_{20}H_{15}O_7N_7$ , separates from alcohol in brilliant yellow crystals, m. p. 154°.

The hydrochloride of the benzylidene derivative,



has m. p.  $175^{\circ}$ ; it cannot be recrystallised, as it readily loses hydrogen chloride. The *sulphate*,  $2C_{27}H_{19}N_7 \cdot H_2SO_4$ , has m. p.  $178^{\circ}$ ; the *nitrate*, m. p.  $166^{\circ}$ ; the *picrate*,  $C_{27}H_{19}O_7N_7$ , crystallises from alcohol in slender, yellow needles, m. p.  $169^{\circ}$ ; the *platinichloride* forms an orange-coloured precipitate, m. p.  $231^{\circ}$ .

*$\alpha\beta$ -Dibenzyl- $\alpha$ -phenylhydrazine hydrochloride,*



crystallises from alcohol, and has m. p.  $186^{\circ}$ ; the corresponding *base*,  $C_{20}H_{20}N_2$ , solidifies slowly, crystallises from ether, has m. p.  $42^{\circ}$ , and decomposes on exposure to the air, giving an odour of benzaldehyde. When boiled with alcohol and mercuric oxide, it is oxidised to phenylbenzylidenehydrazone, and the same product appears to be formed by the action of dilute nitric acid or of picric acid on the base.  *$\beta$ -Benzoyl- $\alpha$ -phenyl- $\alpha\beta$ -dibenzylhydrazine*,  $CHPh \cdot NPh \cdot NBz \cdot CH_2Ph$ , crystallises from alcohol, in which it is readily soluble, and has m. p.  $107^{\circ}$ ; the corresponding *acetyl* derivative,  $C_{22}H_{22}ON_2$ , obtained by boiling the hydrochloride of the base with acetic anhydride, has m. p.  $78^{\circ}$ .

*$\alpha$ -Phenyl- $\alpha\beta$ -dibenzylhydrazine hydrochloride* does not react with potassium cyanate; when boiled for several hours with 20% hydrochloric acid, it yields benzyl chloride and phenylhydrazine.

*Tribenzylhydrazine hydrochloride*,  $CH_2Ph \cdot NH \cdot N(CH_2Ph)_2, HCl$ , obtained by reducing the corresponding benzylidene derivative, or by the action of benzyl chloride on hydrazine hydrate, crystallises from alcohol in compact needles, m. p.  $181^{\circ}$ . When boiled for fifty-six hours with 20% hydrochloric acid, it yields benzyl chloride and hydrazine hydrochloride.

The product obtained by reducing 1-benzylideneamino-2:5-diphenyl-1:3:4-triazole with sodium amalgam and alcohol is diphenyltriazole (Pinner, *loc. cit.*), the *hydrochloride* of which has m. p.  $203^{\circ}$ .

The following generalisations with regard to the decomposition of tertiary hydrazines by boiling hydrochloric acid are given: (1) When the substituents are aryl groups, the hydrazine undergoes a benzidine rearrangement if such be possible. Quaternary hydrazines can, in addition, undergo fission at the  $\equiv N \cdot N \equiv$  union. (2) When the substituents are partly aromatic and partly aliphatic, several reactions are possible. As a rule, the hydrazine with cold hydrochloric acid is transformed into a primary hydrazine and a hydrazone of the hydrazine. When two aliphatic and one aromatic groups are present, heating with 20% hydrochloric acid leads to the formation of the primary aromatic hydrazine and an alkyl chloride (2 mols.). Quaternary hydrazines with two aromatic and two aliphatic substituents undergo fission at the nitrogen linking. (3) Aliphatic hydrazines, as a rule, yield hydrazine and alkyl chlorides. The decomposition of *ac. ecc.*-aliphatic hydrazines and of quaternary aliphatic hydrazines has not been studied.

J. J. S.

**Structure of the Azoxy-compounds.** ANGELO ANGELI and LUIGI ALESSANDRI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 896—900).—*p*-Nitrosoxybenzene prepared by Zinin's method (*Annalen*, 1860, 114, 218) has m. p.  $152^{\circ}$  (Zinin:  $153^{\circ}$ ). *p*-Nitroazobenzene, prepared



from nitrosobenzene and *p*-nitroaniline, forms red laminae, m. p. 135°. Oxidation of this substance with hydrogen peroxide in solution in glacial acetic acid yields a compound, m. p. 148°, which also differs in colour and solubilities from the *p*-nitroazoxybenzene of Zinin. It is suggested that the two substances are isomerides having the formulae  $\text{Ph}\cdot\text{NO}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$  and  $\text{Ph}\cdot\text{N}\cdot\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$  respectively.

R. V. S.

**New Synthesis of *o*-Hydroxyazobenzene.** N. N. VOROSCHTSOFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 787—791).—Although *p*-nitrophenol and *p*-aminophenol do not combine with diazo-salts, *p*-acetylaminophenol readily yields *m*-acetyl-amino-*o*-hydroxyazobenzene. When treated with concentrated hydrochloric acid, the latter easily loses the elements of acetic acid, yielding *m*-amino-*o*-hydroxyazobenzene hydrochloride. On diazotising this with amyl nitrite in glacial acetic acid solution (compare Hantzsch and Jochem, *Abstr.*, 1902, i, 62), a solid diazo-compound is obtained, which, on treatment with boiling alcohol, gives *o*-hydroxyazobenzene in more than 50% yield (calculated on the aminohydroxyazobenzene hydrochloride). This method of preparing *o*-hydroxyazobenzene hence gives much better results than that of Bamberger (*Abstr.*, 1900, i, 531).

*m*-Acetyl-amino-*o*-hydroxyazobenzene,  $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{N}_2\cdot\text{Ph}$ , crystallises from acetic acid in long, straw-yellow needles, m. p. 226°.

T. H. P.

**Action of Substituted Hydrazines on  $\beta$ -Orthotoluquinone.** WILLIAM MCPHERSON and CECIL BOORD (*J. Amer. Chem. Soc.*, 1911, 33, 1525—1531).—In the case of the reaction between *o*-benzoquinone and *as*-acylphenylhydrazines a migration of the acyl group takes place (compare McPherson and Lucas, *Abstr.*, 1909, i, 193), and the conclusion is drawn that the acyl derivatives of the *o*-hydroxyazo compounds, like those of the *p*-series, have the acyl group attached to oxygen, and are therefore represented by the formula  $\text{NPh}\cdot\text{N}\cdot\text{R}\cdot\text{OAcyl}$ .

3:4-Toluquinone is more readily prepared and more stable than *o*-benzoquinone; it reacts with *as*-benzoylphenylhydrazine, forming 4-benzeneazo-*m*-tolyl benzoate. When saponified it yields 4-benzeneazo-*m*-cresol isomeric with the corresponding *p*-cresol described by Nütting and Kohn (*Abstr.*, 1884, 900). The compound undergoes no change when dissolved in ether containing a small amount of fused potassium hydroxide and heated for some hours, a fact which makes it extremely probable that the acyl group is joined to oxygen.

3:4-Toluquinone is a reddish-brown solid, non-volatile, and odourless; it crystallises in clusters of needles, m. p. 70—75° (decomp.). 4-Benzeneazo-*m*-tolyl benzoate (annexed formula) forms orange-yellow needles, m. p. 98°. When saponified with concentrated sulphuric acid, 4-benzeneazo-*m*-cresol is obtained in thin, red plates, m. p. 122°.

4-Tolueneazo-*m*-tolyl benzoate separates in light orange-coloured needles, m. p. 93°.

4-Tolueneazo-*m*-cresol crystallises in thin, lathe-shaped, orange-red crystals, m. p. 148°.

E. F. A.

**Bisulphite Compounds of Hydroxyazo-colouring Matters.**  
 N. N. VOROSCHTSOFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 771—786).

—The author has investigated the structure of the compounds formed by sodium hydrogen sulphite with the following hydroxyazo-colouring matters: benzeneazo-*p*- and -*o*-cresols and benzeneazo-*α*- and -*β*-naphthols. It is found that all hydroxyazo-compounds do not react in the ordinary manner with sodium hydrogen sulphite; thus, *p*- and -*o*-hydroxyazobenzenes and benzeneazo-*o*- and -*p*-cresols undergo no change on prolonged boiling with aqueous-alcoholic sodium hydrogen sulphite solution, whereas the azo-derivatives of *α*- and *β*-naphthol readily react under these conditions, giving crystalline compounds soluble in water. The acetyl derivatives of the two azonaphthols also react with sodium hydrogen sulphite, the compounds obtained yielding, on decomposition with cold dilute ammonia or sodium hydroxide solution, the same hydroxyazo-compounds as are given under similar conditions by the sodium hydrogen sulphite compounds of the non-acetylated azonaphthols; the acetyl groups evidently undergo hydrolysis during the reaction with the sulphite.

The readiness with which these sulphite compounds are decomposed by even dilute alkalis, taken in conjunction with the fact that hydrazobenzene-*N*-sulphonic acid (compare Bucher and Donnenburg, *Abstr.*, 1910, i, 144) gives azobenzene only when heated with sodium hydroxide, is not in agreement with Spiegel's view (*Abstr.*, 1885, 987) that these compounds are hydrazo-*N*-sulphonic derivatives. Then, too, aminoazo-compounds react with sodium hydrogen sulphite, giving products identical with those formed by the corresponding hydroxyazo-compounds; thus, treatment with sodium hydrogen sulphite and subsequently with ammonia affords a simple means for the quantitative conversion of the aminoazo- to the hydroxyazo-compounds of the naphthalene series.

The author regards the compounds formed by sodium hydrogen sulphite with the hydroxyazophenols of the naphthalene series as salts of sulphurous esters, those formed by the benzeneazonaphthols, for example, having the structure:  $\text{NPh} \cdot \text{N} \cdot \text{C}_{10}\text{H}_6 \cdot \text{O} \cdot \text{SO}_2\text{Na}$ .

Although the phenols of the naphthalene series can be readily converted into the corresponding amino-compounds by being heated under pressure with ammonia and ammonium sulphite, thus:  $\text{R} \cdot \text{OH} \rightarrow \text{R} \cdot \text{O} \cdot \text{SO}_2 \cdot \text{NH}_4 \rightarrow \text{R} \cdot \text{NH}_2$ , benzeneazo-*α*-naphthol does not undergo a similar change, the chief product formed under the conditions named being *αα*-dinaphthylamine-bis-azobenzene,



Sodium benzeneazo-*α*-naphthyl sulphite,  $\text{NPh} \cdot \text{N} \cdot \text{C}_{10}\text{H}_6 \cdot \text{O} \cdot \text{SO}_2\text{Na}$ , forms dark yellow needles, and is stable towards cold dilute acids. The corresponding barium salt,  $\text{C}_{12}\text{H}_{10}\text{O}_6\text{N}_4\text{S}_2\text{Ba}$ , forms microscopic, yellow prisms. The yellowish-green copper salt gradually turns brown, free benzeneazo-*α*-naphthol being developed. The same sodium salt is also obtained from benzeneazo-*α*-naphthylamine and sodium hydrogen sulphite.

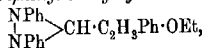
Sodium benzeneazo-*β*-naphthyl sulphite forms shining, golden-yellow needles. The barium salt is yellow, and the characteristic copper salt,  $\text{C}_{12}\text{H}_{10}\text{O}_6\text{N}_4\text{S}_2\text{Cu}$ , forms shining, dark yellow, hexagonal plates.

When benzeneazo- $\beta$ -naphthol is heated with ammonia and ammonium sulphite in a sealed tube at 150–160°, the sulphite compound formed undergoes quantitative conversion into benzeneazo- $\beta$ -naphthol. At temperatures exceeding 200°, new basic products are formed. In the case of the  $\alpha$ -compound, however, change takes place even at 125°, and increases in extent as the temperature is raised; thus, a mixture of sodium benzeneazo- $\alpha$ -naphthyl sulphite, alcohol, and ammonia, heated to 180–200° for twelve hours, yielded a compound,  $C_{22}H_{23}N_5$ , as a violet powder with metallic lustre, m. p. 280°; with concentrated sulphuric acid it forms a dark green solution, which becomes cinnamon-yellow and then reddish-violet on dilution. It dyes wool and cotton violet-red in a faintly acid bath, and thus possesses the properties of a basic, substantive colouring matter. A mixture of benzeneazo- $\alpha$ -naphthol, ammonium sulphite, and ammonia when heated to 130–140° for four hours gave benzeneazo- $\alpha$ -naphthylamine and a violet compound resembling that described above in its general properties, but differing from it in giving with concentrated sulphuric acid a dark violet-blue solution, changing to a reddish-violet colour on dilution. Analogous products are formed at still lower temperatures. T. H. P.

**Hydrazo-compounds. V. Reaction of Hydrazobenzene with Mixed Aldehydes.** BERTHOLD RASSOW and FRITZ BURMEISTER (*J. pr. Chem.*, 1911, [ii], 84, 249–259).—In continuation of previous work (Abstr., 1901, i, 777; 1910, i, 79) the authors have examined the behaviour of hydrazobenzene towards phenylacetaldehyde, cinnamaldehyde, and salicylaldehyde, and find that whilst phenylacetaldehyde and cinnamaldehyde resemble the aliphatic aldehydes in readily condensing with hydrazobenzene, all attempts to effect a condensation with salicylaldehyde proved fruitless.

$\beta$ -Phenylethylidenebis(hydrazobenzene),  $CH_2Ph \cdot CH(NPh \cdot NPh)_2$ , prepared by the interaction of hydrazobenzene and phenylacetaldehyde in alcoholic solution at the ordinary temperature, crystallises in pale yellow needles, m. p. 93–95°, and is readily hydrolysed by dilute acids.

When equimolecular quantities of hydrazobenzene and cinnamaldehyde are heated together in ethyl-alcoholic solution, they yield  $\alpha$ -(or  $\beta$ )-ethoxy- $\beta$ -1:2-triphenyl-3-ethylhydrazinemethylene,



which crystallises in white, prismatic needles, m. p. 135°. It is considered probable that the first stage in the reaction consists in the

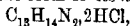
formation of  $\begin{array}{c} NPh \\ | \\ NPh \end{array} > CH \cdot CH : CHPh$ , addition of alcohol subsequent

taking place at the double linking, but experiments undertaken with the object of preparing this compound by the condensation of hydrazobenzene and cinnamaldehyde in ethereal or benzene solution yielded no definite results. Attempts to determine the position of the ethoxy group by hydrolysing the ethoxy-compound with dilute sulphuric acid were also unsuccessful.

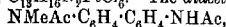
$\alpha$ -(or  $\beta$ )-Methoxy- $\beta$ :1'-triphenyl-3-ethylhydrazimethylene,  $C_{22}H_{22}ON$ , prepared in a similar manner from hydrazobenzene and cinnamaldehyde in methyl-alcoholic solution, crystallises in lustrous, white, rhombic leaflets, m. p.  $163^{\circ}$ . F. B.

**Hydrazo-compounds. VI. Methylhydrazobenzene and Methylbenzidine.** BERTHOLD RASSOW and KURT BERGER (*J. pr. Chem.*, 1911, [ii], 84, 260—277).—*N*-Methylhydrazobenzene,  $NMePh \cdot NPh$ ,

is prepared by heating a benzene solution of hydrazobenzene with methyl sulphate for two days in the presence of magnesium oxide; it crystallises in needles or small, rod-shaped prisms, m. p.  $75^{\circ}$ , and differs from the parent substance in being very stable. When treated with cold strong hydrochloric acid, it yields an intense, dark green solution, from which *N*-methylbenzidine,  $NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NHMe$ , may be isolated in white needles, m. p.  $83^{\circ}$ . The latter compound is, however, best prepared in the form of its hydrochloride,



which crystallises in microscopic leaflets, decomposing at  $250-300^{\circ}$ , by the action of strong hydrochloric acid on methylhydrazobenzene in alcoholic solution. It yields a *picrate*,  $C_{13}H_{14}N_2 \cdot C_6H_3O_7N_3$ , crystallising in yellow, microscopic needles, which decompose at  $167-169^{\circ}$ , and a *platinichloride*,  $C_{13}H_{14}N_2 \cdot PtCl_6$ . The *diacetyl* derivative,



crystallises from alcohol in white, triangular prisms, m. p.  $238^{\circ}$ ; the *dibenzoyl* derivative,  $C_{27}H_{22}O_2N_2$ , in microscopic needles, m. p.  $231-233^{\circ}$ .

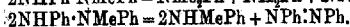
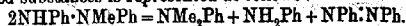
Methylbenzidine condenses with salicylaldehyde, yielding *salicylidene-N-methylbenzidine*,  $NHMe \cdot C_6H_4 \cdot C_6H_4 \cdot N \cdot CH \cdot C_6H_4 \cdot OH$ , m. p.  $194^{\circ}$ , and, when heated with methyl iodide in methyl-alcoholic solution, is converted into tetramethylbenzidine methiodide, m. p.  $263^{\circ}$  (Michler and Pattinson, *Abstr.*, 1882, 199), from which tetramethylbenzidine is obtained by distillation with soda-lime.

Its hydrochloride reacts with two molecules of nitrous acid to form 4-methylnitrosoaminodiphenyl-4'-diazonium chloride, which condenses with dimethylaniline, yielding 4-methylnitrosoaminodiphenyl-4'-azo-p-dimethylaniline,  $NO \cdot NMe \cdot C_6H_4 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot NMe_2$ . This crystallises in microscopic leaflets of a golden lustre, decomposing at  $243^{\circ}$ . It forms a violet hydrochloride, and, when boiled with alcoholic hydrogen chloride, is converted into 4-methylaminodiphenyl-4'-azo-p-dimethylaniline,  $NHMe \cdot C_6H_4 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot NMe_2$ , which crystallises in carmine-red needles, m. p.  $234^{\circ}$ , and forms a hydrochloride,  $C_{24}H_{24}N_4Cl$ .

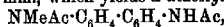
The *azo-dyes* produced by the combination of diazotised *N*-methylbenzidine with  $\beta$ -naphthol-3:6-disulphonic acid and  $\alpha$ -naphthylamine-5-sulphonic acid are respectively red and brown.

The alcoholic mother liquors from the preparation of *N*-methylbenzidine hydrochloride by the action of hydrochloric acid on *N*-methylhydrazobenzene contain 2-(or 4)amino-4'-(or 2')methylaminodiphenyl,  $NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NHMe$ , together with aniline, methyl-

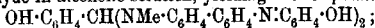
aniline, and dimethylaniline; the formation of the three last-mentioned substances is represented as follows:



The base just mentioned is a strongly refractive, viscid, yellow liquid, b. p.  $255^\circ/25$  mm., which yields a *diacetyl* derivative,



crystallising in rhombic leaflets, m. p.  $327^\circ$ . It condenses with salicylaldehyde in alcoholic solution, yielding the compound,



this has m. p.  $255^\circ$ , and is hydrolysed by boiling dilute sulphuric acid into its components.

F. B.

**Heat Coagulation of Proteins. II. The Action of Hot Water on Egg-albumin and the Influence of Acid and Salts on Reaction Velocity.** HARRIETTE CHICK and CHARLES JAMES MARTIN (*J. Physiol.*, 1911, 43, 1—27. Compare Abstr., 1910, i, 597).—Heat coagulation consists of (1) the reaction between the protein and hot water (denaturation), and (2) the separation of the altered protein in a particulate form (agglutination); (2) occurs more rapidly than (1), and the experiments mainly are concerned with the latter. Denaturation, if means are taken to prevent change in acidity, is a reaction of the first order. As the protein is precipitated, free acid is progressively removed from the solution. Experiments are described which show that egg-albumin fixes acid in the cold, and give the relative amount of acid fixed to the acidity of the solution; the process is reversible. Determinations of the amount fixed during coagulation and its dependence on (1) total concentration of acid, and (2) on hydrogen-ion concentration are given. Salts (sodium chloride and ammonium sulphate) lower the rate of reaction, and up to a certain concentration the effect varies geometrically as the salt is added arithmetically. For the explanations advanced, the original paper must be consulted.

W. D. H.

**The Partial Hydrolysis of Proteins. III. Fibrin Proto-albumose.** PHÉBUS A. LEVESE, DONALD D. VAN SLYKE, and F. J. BIRCHARD (*J. Biol. Chem.*, 1911, 10, 57—71).—The most striking difference between hetero- and proto-albumose is in the amount of glutamic acid on hydrolysis. The former yields 9.51, and the latter 0.63%. Proto-albumose is also poor in valine as compared with hetero-albumose. Any difference in the yield of hexone bases is insignificant.

W. D. H.

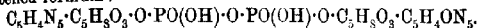
**Hæmochromogen and the Spectroscopic Differentiation of Carboxyhæmoglobin and Oxyhæmoglobin.** FRANZ MICHAEL (*Chem. Zeit.*, 1911, 35, 996).—The author finds that the best reducing agent for changing the colouring matter of the blood into hæmochromogen is an alcoholic, alkaline solution of sodium hypophosphite; a cherry-red coloured solution for the investigation of the absorption spectrum is thus readily obtained at the ordinary temperature, whereas the use of other reducing agents necessitates

warming. Heating the red solution so obtained gradually destroys the hæmochromogen spectrum, the solution becoming yellowish-green, but the addition of a few drops of pyridine to the boiling solution restores the spectrum and further heating has no effect. If the solution, after cooling, is then shaken in the air, the spectrum again disappears, but is reproduced on heating once more.

The sodium hyposulphite reagent may also be used to detect small quantities of carboxyhæmoglobin. After the addition of the hyposulphite to the diluted blood, a few drops of pyridine are added. The colour of the solution changes to an intense yellowish-red, and only the oxyhæmoglobin is changed to hæmochromogen in the cold, the spectrum of carboxyhæmoglobin remaining unchanged. On heating, the carboxyhæmoglobin is changed also into hæmochromogen.

T. S. P.

**The Cleavage of Nucleins in Relation to Enzymes, with Special Reference to the Formation of Hypoxanthine in the Absence of Adenase.** SAMUEL AMBERG and WALTER JONES (*Zeitsch. physiol. Chem.*, 1911, 73, 407—415).—The work of Levene and Jacobs on the intermediate products of hydrolysis of the nucleic acids have led them to consider that the part of the molecule which contains purine substances may be represented by the following shortened formula:



By splitting off phosphoric acid, two nucleosides, guanosine and adenosine, are obtained; the former consists of guanine and  $\alpha$ -ribose, and from it free guanine is obtained by hydrolysis with acids. Adenosine consists of adenine and  $d$ -ribose, and from it free adenine is obtained on hydrolysis. By the action of nitrous acid these two amino-nucleosides are converted into the hydroxy-nucleosides, xanthosine and inosine (hypoxanthosine). Gland extracts produce the same kind of effect by means of enzymes, but different glands act differently; for example, pig's pancreas decomposes nucleic acid with the formation of guanosine, which is not further changed; adenosine, which is simultaneously formed, is changed to inosine as an end product. Pig's liver extract produces from nucleic acid, xanthosine (by deamidation of guanosine), from which xanthine is then formed. The following list of enzymes is given: (1) phosphonuclease, (2) purine nuclease, (3) guanosine-deamidase, (4) adenosine-deamidase, (5) adenase, (6) guanase, (7) xanthosine-hydrolase, (8) inosine-hydrolase, and (9) xantho-oxydase.

The present experiments show that phosphonuclease and purine-nuclease, which respectively split off phosphoric acid and purine bases, are independent enzymes. Dog's liver can split off phosphoric acid from nucleic acid, but cannot split off adenine from the adenosine so formed; no adenine is found among the products, and it would be if it were formed, since the dog's liver contains no adenase to convert it into hypoxanthine. Nevertheless, dog's liver extract splits off hypoxanthine quantitatively from thymus-nucleic acid; this is because the adenosine formed is deamidised to inosine, and this is hydrolytically split so as to yield hypoxanthine.

W. D. H.

**The Application of the Optical Method to a Study of the Enzymatic Decomposition of Nucleic Acids.** SAMUEL AMBERG and WALTER JONES (*J. Biol. Chem.*, 1911, 10, 81—87. Compare Pighini, this vol., ii, 236).—Extracts of organs freed from blood produce the same results as those containing blood; their varying activities on nucleic acids are therefore not due to blood or blood-serum. By the optical method no change was observed in the rotation of thymus-nucleic acid under the influence of serum. Yeast-nucleic acid, however, does suffer a diminution in rotatory power, as Pighini stated, but this does not mean liberation of either phosphoric acid or purine bases. Rotation is also lowered as the temperature rises, and returns to its previous value on cooling. Pighini's results must therefore be accepted with caution. W. D. H.

**A Method for the Study of Proteoclastic Enzymes.** PHILIP ADOLPH KOBER (*J. Biol. Chem.*, 1911, 10, 9—14).—Amino-acids (six were tested) form copper salts that yield their copper as hydroxide when boiled with a slight excess of alkali. The polypeptides and peptones tested which form copper salts do not yield their copper as hydroxide when treated in the same way. The method is suggested as one for distinguishing the two classes of substances in digests. W. D. H.

**The Mechanism of Proteoclastic Enzymes.** AUGUSTE FERRACH and MARCEL SCHOEN (*Compt. rend.*, 1911, 153, 133—136).—A greater proteoclastic action is produced in the presence of mono-potassium phosphate than in that of the dipotassium salt by papayotin, pancreatin, and the proteoclastic enzyme of *Tyrophlic tenuis*, acting on fibrin, caseinogen, and other proteins. This difference is due mainly to the reactions of the media. When pancreatin is incubated with a solution of potassium or sodium phosphate, an increase in activity is produced. W. J. Y.

**The Behaviour of Phenolase towards Acids.** ALEXIS BACH and B. SBAESKY (*Biochem. Zeitsch.*, 1911, 34, 473—480).—The phenolase was prepared from *Lactarius vellereus*, and its action on pyrogallol was determined by estimating quantitatively the purpurogallin formed. This was done by filtering it off from the solution, dissolving it in concentrated sulphuric acid, and titrating the solution thus obtained, after dilution with water, with 0.01N-permanganate solution. In addition to this, the amount of pigment formed, which remains in solution after removing the purpurogallin, was estimated colorimetrically. It was found that the presence of small quantities of acid accelerated the action of phenolase. With increasing quantities of acid, the amount of purpurogallin diminishes, but that of the soluble pigment increases. At the limit at which the purpurogallin formation ceases, however, the amount of soluble pigment commences to diminish. The amount of the toxic dose of acid, however, is so great in comparison with the amount of ferment that there can be no question of the acid merely acting on a manganese or other metallic compound. By varying phenolase concentrations on the same substrate, the toxic

tion of the acid is proportional, not to the absolute phenolase content, but to its activity under the given conditions. The authors draw the conclusion that their results do not accord with Bertrand's theory of phenolase action.

S. B. S.

**Preparation of Pure Invertase.** HANS EULER and SIXTEN JULLBERG (*Zeitsch. physiol. Chem.*, 1911, 73, 335—344).—Invertase prepared by autolysis (O'Sullivan and Thompson, *Trans.*, 1890, 57, 34) was purified by solution in water and precipitation with an equal volume of alcohol. Invertase is precipitated with colloidal iron only when other impurities, particularly electrolytes, are also present. The most active preparations were obtained by precipitation of the autolysed liquor with lead acetate, removal of the lead as sulphide, and of the protein by rubbing the filtrate with much kaolin; a final precipitation with alcohol gave an invertase of great activity. This contained 4.7% of nitrogen, which was lessened by diffusion to 1.85%. Molecular-weight determinations based on the rate of diffusion gave a value of 27,000. During diffusion about 25% of impurities of lower molecular weight are separated, and the activity of the invertase correspondingly increased. The activity of the purified invertase was directly proportional to the weight used.

E. F. A.

**Yeast-Gum.** E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1911, 73, 314—316. Compare Euler and Fodor, this vol., i, 607).—Polemic. Invertase is perhaps the magnesium salt of an acid containing nitrogen and phosphorus; it is not a protein. A plea is made for the continuance of the term invertin instead of invertase. The suggestion of Euler and Fodor that invertase is a complex carbohydrate related to yeast-gum is negatived; active preparations containing no trace of yeast-gum have been obtained frequently.

E. F. A.

**Influence of the Reaction of the Medium on the Activity of Cellase.** New Character Distinguishing it from Emulsin. ABRIEL BERTRAND and ARTHUR COMPTON (*Compt. rend.*, 1911, 153, 360—363. Compare Abstr., 1910, i, 212, 290, 800; this vol., i, 592).—The diastase from sweet almonds capable of hydrolysing cellulose functions best in a medium having almost the same reaction as that of the natural preparation, namely, alkaline to methyl-orange and acid to phenolphthalein, corresponding with a concentration in hydrogen ions of  $10^{-8.2}$ . Addition of more than a trace of acid inhibits the diastatic activity. Cellase in this respect differs from emulsin, which shows maximum activity only in solutions alkaline to phenolphthalein.

W. O. W.

**Heat Resistant Lipase.** N. L. SÖHNGEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 166—170).—The lipase produced by *Bacterium fluorescens liquefaciens*, *B. pyocyaneum*, *B. punctatum*, and *B. liquefaciens* is capable of withstanding a temperature of 100° for five minutes without being rendered inactive, whilst that formed by *Bacterium polyticum*, *B. Stutzeri*, *B. fluorescens non-liquefaciens*, *Oidium lactis*,



*Aspergillus niger*, *Penicillium glaucum*, and *Cladosporium butyri* is destroyed at 80°.

The two enzymes also differ in their relation to small quantities of acid; ordinary lipase is inhibited only when the reaction of the medium is *N*/50-acid, whereas the heat resisting lipase is rendered inactive at *N*/100-acid.

H. B. H.

**The Chemical Occurrences in Milk Curdling by Rennet.**  
IVAR BANG (*Skand. Archiv. Physiol.*, 1911, 25, 105—144).—Rennet converts the caseinogen of milk into casein, and the latter is then united to calcium phosphate to form the curd. In the thirty or forty years since this was established by Hammarsten little or nothing has been added, especially in relation to the intermediate stages in the reaction. After the addition of rennet, milk remains apparently unaltered for minutes or hours, and then, suddenly, coagulation takes place. It is the object of the present research to ascertain what is occurring before the last step, the actual curdling, is seen. Some of the experiments were performed with milk, and some with solutions of caseinogen prepared by Hammarsten's method. Rennet is destroyed by momentary heating to 65°, and milk is not changed at this temperature. By adding rennet fractionally, summation is noted; for example, the coagulation time on adding 0.1 c.c. of rennet to 10 c.c. of milk was eight minutes, and on adding 0.2 c.c. four minutes; if, however, 0.1 c.c. is added, and four minutes later another 0.1 c.c., then clotting occurs two minutes after the second addition. If, however, the milk after the first addition is heated to 65°, no such summation is seen; and if the second dose of rennet is not added until four minutes after the heating and subsequent cooling, the coagulation time is lengthened. Although the milk had not curdled in the interval, it had undergone certain changes, due to the first addition of rennet and to the heating of the mixture. If a caseinogen solution is boiled, cooled, and then rennet and calcium chloride added, the coagulation time is also shortened, especially in experiments in which any suspended calcium carbonate (used in the preparation of the solution) is removed by centrifugalising. The so-called solution of caseinogen prepared by Hammarsten's method is really a solution of caseinogen united to calcium carbonate; rennet alone does not curdle it; the addition of calcium chloride or phosphate is also necessary; the original solution is opalescent, but clears on the addition of a little sodium chloride; but heating after the addition of this salt restores the opalescence, and this is reversible on alternate heating and cooling. At a high temperature caseinogen has therefore a greater affinity for calcium carbonate than for alkali; at a low temperature this is reversed. The actual curdling is due to the formation of a compound between the caseinogen-calcium carbonate and other calcium salts, such as the chloride or phosphate, and the numerous experiments, both with caseinogen solution and milk, show differences in action between the chloride and the phosphate. The suggestion that these latter salts act as activators of the enzyme was examined and negatived. The longer the enzyme has acted previous to the addition of the calcium chloride, the more rapidly does curdling occur after the addition. Rennet does not produce only

change in the caseinogen of the milk, but has also something to do with the mobilisation of the calcium salts. Further experiments, which are difficult to summarise shortly, lead to the conclusion that calcium chloride by its osmotic pressure inhibits the dissociation of the caseinogen-calcium carbonate-calcium chloride compound, and the undissociated compound is precipitated; an excess of phosphate, on the other hand, inhibits precipitation; calcium phosphate is insoluble in water, and so cannot affect osmotic pressure; it forms an insoluble compound with the caseinogen; the avidity of caseinogen for calcium salts rises with temperature.

Milk itself contains, in addition to caseinogen, other proteins and salts; the lactose is indifferent to curdling phenomena. The salts are alkali chloride, phosphate and carbonate, and calcium citrate. The influence of the salts is discussed at length with numerous experiments. Calcium citrate favours, alkali citrate inhibits, curdling; the former gives up calcium, the latter removes it from the milk. The effect of milk-serum on the process did not give constant results. Crystalline egg-albumin (and serum-albumin to a less degree) inhibits the process, but this is in part due to the alkali used in neutralising the solution. Egg-white and serum act in the same way. Lact-albumin acts similarly, and colostrum, which is very rich in lact-albumin, has a very strong inhibitory action. This action in all cases is not on the activity of the enzyme in changing caseinogen, but on the final act of curdling. Rennet action is thus very complex; the calcium salts of the milk are partitioned between organic and inorganic acids and the various milk proteins; the caseinogen takes up more and more calcium phosphate long before it is united, sufficient to cause precipitation to occur. There are probably several phases in the formation of casein, and several more in the combination of casein with calcium phosphate. It is doubtful whether rennet should be classed with coagulating enzymes, for rennet does not in itself produce curdling, and the final act of curdling is not true coagulation, but is more akin to the precipitation of protein by neutral salts. Casein itself is capable of re-solution, and can be re-curdled with rennet under appropriate conditions.

The nomenclature adopted in the preceding abstract is that usually adopted in this country. In the original German, caseinogen and casein are spoken of respectively as casein and paracasein. W. D. H.

**Further Observations on Rennin and Pepsin in the Gastric Juice of the Calf.** A. RAKOCZY (*Zeitsch. physiol. Chem.*, 1911, 73, 53-458).—This is a continuation of the author's previous work (*Abstr.*, 1910, i, 801), in which he found that milk curdling is produced by two enzymes in the calf's gastric juice, namely, by pepsin, and by a special milk-curdling enzyme, rennin (chymosin). With increase of age, the latter disappears, but there is no ground for believing that there is any difference in the pepsin of animals of varying ages. W. D. H.

**Amylases. III. Preparation and Properties of Pancreatic Amylase.** HENRY C. SHERMAN and M. D. SCHLESINGER (*J. Amer. Chem. Soc.*, 1911, 33, 1195-1204. Compare *Abstr.*, 1910, ii, 1012; 799).—Having been much hampered in previous work by the

deterioration of amylolytic power in pancreatin solutions, the authors have examined the influence of different solvents and precipitants on the amylolytic activity of commercial pancreatin, and find that it is fairly permanent in 50% alcohol, the pancreatic amylase being recovered in active form from the solution by precipitation with strong alcohol or a mixture of alcohol and ether. By a process involving extraction of dry pancreas powder with 50% alcohol, repeated precipitation, and purification by dialysis in 50% alcohol, preparations having diastatic powers up to 3480 on the new scale (Abstr., 1910, i, 799) have been obtained, corresponding with over 5000 on Lintner's scale, and with  $D_{50}^{\circ} = 500,000$  on Wohlgemuth's scale. Six independent preparations showed in the dry substance activities of 3310, 3670, 3540, 3570, 3720, and 3320. This agreement indicates that these preparations are substantially alike, and that the process yields a fairly definite result. The product has a composition and the characteristic reactions of a protein closely resembling Osborne's malt diastase.

The pancreatic amylase thus prepared, acting at 40° on soluble starch made by Lintner's method, formed 6000 times its weight of maltose in twenty minutes, and 211,000 times its weight in thirty hours. It digested 400,000 times its weight of starch to the "erythro-dextrin stage" in less than twenty-two hours, and to products giving no reaction with iodine in forty-eight hours. C. S.

**Catalase.** OSKAR LOEW (*Biochem. Zeitsch.*, 1911, 34, 354).—A claim for priority in reference to the action of nitrates on, and the detection of, catalase. S. B. S.

**Extraction of Zymase.** ALEXANDRE LEBEDEF (Bull. Soc. chim., 1911, [iv], 9, 744—750).—Reply to Kayser (compare this vol., ii, 640). The author has systematically studied the factors influencing the activity of the zymase preparation, namely, the temperature and the time of fermentation, the condition and kind of yeast, the method of preservation of the juice, etc. The top yeast, called "parisienne," does not give an active juice either by the process of Lebedeff or by that of Buchner. W. G.

**Is Zymase a Diastase?** ALEXANDRE LEBEDEF (Bull. Soc. chim., 1911, [iv], 9, 672—682; *Ann. Inst. Pasteur*, 1911, 25, 682—684).—From experiments with an extract made by macerating dried yeast for two hours with three volumes of water, the author finds that the zymase contained in it is a typical diastase. The quantity of sugar fermented, however, is nearly proportional to the amount of co-enzyme present, provided that this is not less than 20%. The unusual activity of the extract prepared by the author's method is due to the amount of co-enzyme contained in it. It is suggested that yeast is more active than any of its extracts, not because it contains more zymase, but because as fast as co-enzyme is destroyed during the fermentation, it is produced again by cellular activity. R. V. S.

## General and Physical Chemistry

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**The Theory of Refraction Constants.** OTTO WIENER (*Ber. K. Sachs. Ges. Wiss. Math.-phys. Kl.* 62, 1910, 256—277).—Mathematical; the author obtains for the dielectric constant of a mixture consisting of one substance imbedded in another a generalised Lorenz-Lorentz expression which involves a "form-number"  $u$ . This number is determined by the shape of the imbedded particles, and is greater than 2 when the particles are not spherical. The values of  $u$  in different cases are discussed; it is shown also how they may be derived from optical data. The results obtained for different substances correspond in general with their relative molecular complexities. The advance with respect to previous empirical improvements of the Lorenz-Lorentz formula consists in the mode of deduction and the theoretical interpretation of the quantity  $u$ . F. M. G. M.

**Refractive Index of Water.** GREGORY P. BAXTER, LAURIE LORNE BURGESS, and HERBERT WILKENS DAUDT (*J. Amer. Chem. Soc.*, 1911, 33, 993—991).—In connexion with a study of the refractive indices of salt solutions and the refractive constants of dissolved salts (following abstract), a knowledge of the exact value of the index of refraction of water at 25° was required. Determinations of the constant have, therefore, been made at this temperature, and also at 20° and 30°, special attention being devoted to the purity of the water and the careful regulation of the temperature. The values obtained for  $[n]_D$  are 1.33299 at 20°, 1.33248 at 25°, and 1.33190 at 30°, when referred to air at the same temperatures, and 1.33335 at 20°, 1.33284 at 25°, and 1.33225 at 30°, when referred to vacuum. These values are probably correct within 0.00002. E. G.

**Refractive Power of the Halogen Salts of Lithium, Sodium, and Potassium in Aqueous Solution.** GREGORY P. BAXTER, ARTHUR C. BOYLSTON, EDWARD MUELLER, N. HENRY BLACK, and PHILIP B. GOODE (*J. Amer. Chem. Soc.*, 1911, 33, 901—922).—Much work has already been done on the refractive indices of solutions of electrolytes, but the accuracy of most of the results is regarded as doubtful, insufficient care having been taken, in many cases, to ensure the freedom of the substances from probable impurities, especially moisture.

The densities and refractive indices of solutions of the chlorides, bromides, and iodides of lithium, sodium, and potassium have been determined at 25° at various concentrations.

The increase in density of the solutions with increasing concentration is nearly, but not quite, proportional to the quantity of salt in unit volume. The values obtained by dividing the differences between the densities of the solutions and of water by the molal concentrations have been calculated. These increments decrease slowly with increasing concentration, except in the case of lithium iodide. This

decrease is due to the contraction which takes place during the solution of most salts in water, lithium bromide and iodide being exceptions to the rule and showing expansion during solution.

Similar increments have been calculated for change in the refractive index, and these also decrease slowly as the concentration increases. The increments are closely additive at equivalent concentrations, especially at low concentrations, indicating that the ionic, but not the molecular, increments are nearly constant. The increments for potassium salts are uniformly lower than those for sodium salts, whilst those for lithium salts are the lowest; this peculiarity is doubtless closely connected with the contraction or expansion which takes place when the salts are dissolved.

It is pointed out that a refractive constant for one component of a solution cannot be entirely satisfactory, if calculated on the assumption that the specific refraction of the other component remains constant in solution and equal to that of the pure substance, since, in general, specific rotation changes with even slight changes of conditions. The specific refractions of the nine salts are nearly constant, but increase slightly as the dilution increases. The molecular refractions are nearly additive at all concentrations.

E. G.

**Second Spectrum of Hydrogen in the Extreme Red.** F. CROZE (*Compt. rend.*, 1911, 152, 1574—1576).—The position and relative intensity of 72 bands in the secondary spectrum of hydrogen in the extreme red have been measured for wave-lengths beyond  $\lambda$  656 Ångström units. The results, which are given in tabular form, show no well-defined regularities in the distribution of the lines. The most intense are situated at  $\lambda$  7072, 7325, 6916, and 7056. W. O. W.

**Spectroscopy of Oxygen.** WALTER STEUBING (*Ann. Physik*, 1911, [iv], 34, 1003—1010).—Polemical against Kayser (this vol., ii, 237). H. M. D.

[Spectroscopic Investigations.] JOHANNES STARK (*Ann. Physik*, 1911, [iv], 34, 1011—1014).—Polemical against Kayser (this vol., ii, 237). H. M. D.

**Spectrum of Air Given by the Initial Discharge of the Spark with Self-induction.** GUSTAVE A. HEMSALECH (*Compt. rend.*, 1911, 152, 1471—1474. Compare this vol., ii, 449).—The true spark spectrum of air has been shown to differ from the spectrum produced by the oscillations following the spark. The former may be rendered more intense by blowing air across the electrodes, thus raising the potential. The intensity of the spectrum due to the initial discharge of a self-induction spark varies inversely as the capacity of the condenser and directly as the self-induction. W. O. W.

**Mineral Constituents of a Dusty Atmosphere.** W. NEZ HARTLEY (*Proc. Roy. Soc.*, 1911, A, 85, 271—275).—Photographs of

spark spectra between cadmium electrodes have been taken with exposures varying from one to sixty seconds. In the case of the longer exposed plates, the solar spectrum is overlaid by exceedingly fine dark lines, which are due to solid matter suspended in the atmosphere. Twenty-two such lines have been identified as those of elements known to be contained in atmospheric dust, namely, calcium, lead, copper, iron, manganese, nickel, magnesium, and carbon. Spectra of the spark discharge in hydrogen showed no trace of these lines. Determinations of the weight of material necessary to give the lines of these spectra have also been made. From these it appears that the calcium and copper reactions are more delicate than the test for sodium by the yellow flame or even by the photography of the ultimate lines of sodium in the oxyhydrogen flame and spark. The reactions of lead, manganese, and magnesium in the spark are much more sensitive than those of sodium, calcium, or copper. H. M. D.

**Regularities in the Spectrum of Neon.** HERBERT E. WATSON (*Proc. Camb. Phil. Soc.*, 1911, 16, 130—135).—From an examination of the spectrum of neon it is found that, if the bright lines only are considered, the spectrum exhibits three groups of lines which diminish in general intensity towards the ultra-violet end of the spectrum.

The first group, which extends from the extreme red to  $\lambda = 4071$ , consists of one very bright line, one weaker line, three quadruplets, and three triplets. The second group, extending from  $\lambda = 3754$  to  $\lambda = 3370$ , contains one very bright line, one weaker line, three quadruplets, and four triplets, whilst the third group, extending from  $\lambda = 3167$  to  $\lambda = 2736$ , contains two bright lines, three quadruplets, and ix (or possibly only five) triplets. The differences between the frequencies of the first and second, first and third, and first and fourth lines in the systems of quadruplets are respectively 1070, 1429, and  $847 \times 10^6/\lambda$ .

The arrangement of the lines resembles closely the blue portion of the red argon spectrum investigated by Rydberg. H. M. D.

**The Separation of the Spectral Lines of Calcium and Strontium in the Magnetic Field.** B. E. MOORE (*Physikal. Zeitsch.*, 1911, 12, 443—445).—From measurements of the separation of the lines of calcium and strontium under the influence of a strong magnetic field, it is found that Preston's law is not satisfied in the majority of cases. For both elements, however, the lines of the second subsidiary series and the first lines of the first subsidiary series are solved in accordance with the requirements of this law.

H. M. D.

**Vacuum Tube Spectra of Mercury.** FRANK HORTON (*Proc. Roy. Soc.*, 1911, 4, 85, 288—302).—Experiments with mercury vacuum tubes are described, which show that several spectra can be obtained which depend on the electrical conditions of the discharge. The particular spectrum appearing in a given case depends on the energy of the discharge in relation to the mass of vapour through which it

passes. The simplest spectrum consists of five lines, and this is always obtained when both limbs of the tube are fairly hot and the discharge is running easily. As the energy of the discharge is increased or the pressure of the vapour diminished, more complicated spectra make their appearance. All the lines of each spectrum appear at the same moment as the electrical conditions become suitable to its production.

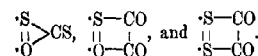
Two of the methods employed for producing different spectra of mercury are referred to as being of particular significance for spectroscopic purposes. In one of these, discharge takes place under a low potential difference with the aid of a glowing lime cathode, whilst in the other, discharge is effected in an electrodeless ring by electro-magnetic induction.

H. M. D.

**The Absorption Spectra of the Vapours of Some Sulphur Compounds.** JOHN E. PURVIS (*Proc. Camb. Phil. Soc.*, 1911, 16, 155—160. Compare *Trans.*, 1910, 97, 2287).—Observations relating to the absorption spectra of the vapours of ethyl trithiocarbonate, diethyl thionthiocarbonate, ethyl thioloalate, and propyl dithioloalate are recorded which show the influence of temperature between about 15° and 100°, and of pressure between about 760 mm. and 950 mm.

Each of the vapours exhibits one large absorption band which widens as the temperature and pressure are increased. This band is comparable with that previously found in alcoholic solution, although the latter lies nearer the less refrangible end of the spectrum. There is no formation of series of narrow bands analogous to those found in the vapour of carbon disulphide. The broad absorption band is supposed to be due to a ring structure, and the four compounds examined

are represented as containing respectively the ring forms:  $\begin{array}{c} \cdot S \\ \diagup \quad \diagdown \\ \cdot S \end{array} > CS$



H. M. D.

**Investigation of Emission Spectra of Solid Aromatic Substances by means of the Ultra-violet Filter.** ERON GOLDSTEIN (*Ber. Deut. physikal. Ges.*, 1911, 13, 378—392. Compare *Abstr.*, 1904, ii, 689, 690; 1910, ii, 469, 671).—The ultra-violet filter described by Wood can be conveniently employed in the investigation of the emission spectra of substances which are excited by radiation of very short wave-lengths. It is found that a large number of aromatic compounds, under the influence of the ultra-violet rays thus obtained, exhibit discontinuous emission spectra which are identical with the initial spectra which appear as the first and transient result of the action of cathode rays. Excitation by ultra-violet rays affords therefore a means of studying the detailed structure of the initial spectra. When aromatic ketones or aldehydes are acted on by cathode rays, the chief spectrum is developed immediately, and no evidence of an initial spectrum is obtained. A similar result is found in the action of the ultra-violet rays on these substances.

As with the cathode rays, many aromatic compounds give rise to after-glow spectra (solution spectra) when the ultra-violet rays cease to act. These spectra, the intensity of which increases as the temperature falls, are in all probability due to the presence of traces of impurities. Fractionation experiments are described in support of this view.

When the chief spectrum of a substance has been developed by the action of cathode rays, and the substance is then acted on by ultra-violet rays, these give rise to the chief spectrum instead of the initial spectrum. This indicates that the original substance is modified by the action of the cathode rays, and that the chief spectrum is due to the transformed substance.

The fact that certain substances give emission spectra when acted on by cathode rays, but not when subjected to ultra-violet rays from the filter, is probably due to the remote position occupied by the region of selective absorption in the ultra-violet. Rays of such small wave-length are not transmitted by the filter. H. M. D.

**Some Causes of the Formation of Colour in Inorganic Compounds.** C. REICHARD (*Pharm. Zentr.-h.*, 1911, 52, 591—597).—

A discussion of the colour of inorganic compounds as compared with the colour of the elements from which they are built up. The effect of temperature, state of division, etc., on the variation in colour is dealt with, but no explanation of the colours is given.

T. S. P.

**The Colorimetric Dilution Law and its Application to Triphenylmethyl.** JEAN PICCARD (*Annalen*, 1911, 381, 347—351).

—According to Beer (*Ann. Phys. Chem.*, 1852, 86, 78), the observed intensity of a coloured solution as observed by looking down on the solution placed in a cylinder does not alter during the addition of more of the solvent. The same law holds good when the dissolved material consists of two isomeric modifications in equilibrium with one another. The ratio of the concentrations of the two forms is constant, and hence the colour is constant and independent of the dilution  $I/C^2 = K$ . When, however, the one modification is a dissociating polymeride of the other, the relationships are different; then  $C/c^n = K^1$ . With increasing dilution the value of  $C$  diminishes more rapidly than the value of  $c$ .

When solutions of triphenylmethyl in absolute ether are examined in the colorimeter, it is noticed that the yellow colour of the solution increases in intensity during dilution up to a certain maximum value. The colourless triphenylmethyl is presumably a polymeric form of the yellow unimolecular form (compare Schmidlin, *Abstr.*, 1908, i, 623).

J. J. S.

**Absorption of Light of Some Corresponding Ethane, Ethylene, and Acetylene Derivatives.** HANS STOBBE and ERICH EBERT (*Ber.*, 1911, 44, 1289—1294).—The authors have investigated the ultra-violet absorption spectra of the following groups of compounds in alcoholic solution, and find that the replacement of a single linking by a double



or triple linking causes, in all groups, a displacement of the absorption bands (or, in the case of continuous absorption, of the absorbed region) towards the visible spectrum, but the effect in the case of a triple linking is not so great as that of a double linking: (1) Ethylbenzene, styrene, phenylpropionic acid; (2)  $\beta$ -phenylpropionic, phenylpropionic and the stereoisomeric cinnamic acids; (3) phenyl phenyl-ethyl ketone, phenyl styryl ketone and phenyl phenylacetylene ketone; (4) dibenzyl, stilbene and tolane; (5) diphenylbutane, diphenylbutadiene, diphenyldiacetylene and diphenylbuteninene.

The formation of reduction or additive products from acetylenic compounds, whereby the triple linking is converted into an ethylenic linking, is therefore accompanied by a deepening of the colour, and the same is true of the formation of polymerisation products.

The polymerisation of phenylpropionic acid to 1-phenylnaphthalene 2:3-dicarboxylic acid causes a displacement of the limits of absorption towards the visible spectrum, by about 700 oscillation frequencies.

F. B.

**Fluorescence and Radioluminescence of Some Hydrocarbons with Ethane, Ethylene, and Acetylene Residues.** HANS STOBBE and ERICH EBERT (*Ber.*, 1911, 44, 1294—1297).—The fluorescence and radioluminescence of (1) dibenzyl, stilbene and tolane, and (2) of diphenylbutane, diphenylbutadiene, diphenylbuteninene and diphenyldiacetylene have been investigated, and it is found that in the same series, hydrocarbons containing only single or triple linkings have approximately the same luminescence, whilst those containing double linkings show a much higher luminescent power. Thus, in the second series, the intensity of luminescence increases from the butane and diacetylene derivatives to a maximum with the butadiene compound, the luminescence of diphenylbuteninene having an intermediate value.

The effect accompanying the replacement of a single by a double linking is therefore much greater than that produced by the triple linking, which raises the power of luminescence to only a small extent.

The authors point out a connexion between the intensity of luminescence and the position and form of the ultra-violet absorption bands; increase in the intensity of luminescence is accompanied by a deepening of the absorption bands and their displacement towards the visible spectrum (compare preceding abstract).

F. B.

**Stokes' Law and a General Relation between Absorption and Phosphorescence.** L. BRÜNINGHAUS (*Compt. rend.*, 1911, 152, 1578—1580. Compare Abstr., 1910, ii, 88, 89).—A comparison of all the known absorption and emission spectra of organic and inorganic phosphorescent substances has shown that each group of bands of the emission spectrum is nearer the red than the corresponding and adjacent group of the absorption spectrum. In this respect phosphorescent substances are in accord with the requirements of Stokes' law.

W. O. W.

Triboluminescence. P. N. VAN ECK (*Pharm. Weekblad*, 1911, 48, 581—588, 611—614, 654—665).—A summary of published work on triboluminescence. A. J. W.

Electrical Double Refraction of Carbon Compounds. RICHARD LEISER (*Chem. Zentr.*, 1911, i, 622—624; from *Abhandl. Deut. Bunsen Ges.*, 1910, No. 4, 1—71).—According to Kerr's formula the difference in path,  $\Delta$ , expressed in terms of wave-lengths, between the ordinary and extraordinary rays in the case of electrical double refraction is given by the formula  $\Delta = B/E^2$ , where  $l$  is the distance in centimetres between the condenser plates used in the interference method of measurement,  $E$  is the strength of field, and  $B$  is the characteristic constant for the substance under investigation. In the case of carbon disulphide, which is used as the standard substance of comparison in this investigation, as well as for many other substances,  $B$  is approximately proportional to  $1/\sqrt{\lambda}$ , where  $\lambda$  is the wave-length.

About 150 organic liquids have been investigated, the ratio of  $B$  to  $B_0$  (the latter being the constant for carbon disulphide), being determined under different conditions of field strength, temperature, kind of light used, etc. A full description of the apparatus and method of measurement is given. Most of the data hold for room temperature, but in a few cases measurements were made over a temperature interval of 20°. The great variation in the behaviour of isomerides is illustrated by the following table, which gives the values of  $100 B/B_0$ :

n-Butyl alcohol .....	-113	Benzyl alcohol .....	-477.0
iso-Butyl alcohol .....	-137	m-Cresol .....	+657.0
tert.-Butyl alcohol.....	+154	Anisole.....	+35.5

No other physical property of organic liquids varies between such wide limits, and it is impossible to determine the atomic values of this property, as, for example, in the case of refractivity, etc. The value of  $B$  is very sensitive towards temperature, generally decreasing about 0.5% per degree, so that a comparison of the values obtained at room temperatures is somewhat arbitrary. Nevertheless, the value of  $B/B_0$ , excepting in the case of compounds such as nitroform, is fairly independent of the temperature. In some cases, for the purpose of comparison, the molecular electrical double refraction,  $MB/B_0d$ , is calculated, but generally the author deals only with the ratio  $100 B/B_0$ .

For the hydrocarbons this ratio is always positive, generally small, and increases with the molecular weight; the symmetrical compounds give the smallest values. The following values of  $100 B/B_0$  have been obtained: benzene, 12.1; toluene, 24.3; ethylbenzene, 25.6; o-xylene, 41.2; m-xylene, 24.4; p-xylene, 22.6;  $\psi$ -cumene, 30.7; and mesitylene, 18.7. The saturated paraffins have especially small constants, which diminish as the chain becomes more branched; open and cyclic paraffins show very little differences. Each double linking increases the constants 6—9 units. Substitution of a hydrogen atom by a negative group greatly increases the constant: fluorobenzene, 191; chloro-

benzene, 385; bromobenzene, 574; iodobenzene, 288; nitrobenzene, 10070; methyl iodide, 209; nitromethane, 330.

The following numbers for different alcohols illustrate the large effect of the introduction of the OH-group: methyl alcohol, 30; ethyl alcohol, about 0; *n*-propyl alcohol, -78; *n*-butyl alcohol, -113; isopropyl alcohol, 73; benzyl alcohol, -477; *tert*-butyl alcohol, 134; *m*-cresol, 657.

The ethers are generally more negative than would be calculated from the means of the alcohol values; in most cases the constants are small, whereas those of the aldehydes and ketones are very large and positive: acetone, 505; acetophenone, 2060; benzaldehyde, 2490. Paraldehyde has a negative constant, -713, indicating the presence of ether linkings.

The fatty acids have small positive constants, the values of which are practically independent of the molecular weight in the higher members of the series; there is also a periodic rise and fall in the constants, similar to that observed in the case of the freezing points. This periodicity is found in several classes of compounds, as, for example, in the substituted aromatic hydrocarbons, whilst in the poly-substituted aromatic compounds definite regularities are observed. With increasing substitution in the paraffins, the constant first increases greatly, then diminishes rapidly to a large negative value, and finally approaches the original small positive value, as illustrated by: methane, about 12; methyl chloride, 200-300; methylene chloride, -36; chloroform, -100; carbon tetrachloride, 2.3.

Substances with high constants are the most reactive, those with low constants being slow to react. There are exceptions, however, as in the case of phenylhydrazine, the constant for which is almost zero. The constants are of great use in determining questions of constitution, and they show also a connexion with the dielectric constant.

The author connects his results with the electron theory of electro-optical effects. There is much to indicate that the individual molecules are anisotropic structures, which, contrary to what holds in the case of crystals, can assume all possible positions with respect to each other

T. S. P.

**Radiations Decomposing Water and the Extreme Ultra-violet Spectrum of the Mercury Arc.** A. TIAN (*Compt. rend.*, 1911, 152, 1483-1485. Compare this vol., ii, 452).—The radiations decomposing water with formation of hydrogen and hydrogen peroxide are localised in the extreme ultra-violet, beyond  $\lambda$  1900 Ångström units. The light from a quartz mercury lamp brings about this decomposition principally through the presence of the rays  $\lambda$  1846, 1848, and 1851. An electric spark between aluminium electrodes emits the rays  $\lambda$  1854, 1857.5, and 1862, and is also able to decompose water in the same way.

W. O. W.

**Photocatalysis. Action of Light on Mixtures of Uranium Salts and Oxalic Acid.** LUDWIK BRUNER and J. KOZAK (*Zeitsch. Elektrochem.*, 1911, 17, 354-360).—Solutions containing uranyl nitrate and oxalic acid are exposed to strong daylight, a number of

solutions being exposed simultaneously so as to obtain comparable results. The reaction is too slow in artificial light. Two reactions take place:  $C_2O_3(OH)_2 = CO_2 + CO + H_2O$  and  $C_2O_3(OH)_2 = CO_2 + H \cdot CO \cdot OH$ , about 27% of the decomposition being due to the second. The addition of strong acids to the solution has no effect on the reaction. The rate of decomposition of the oxalic acid is independent of its concentration within wide limits. It increases with the concentration of the uranyl salt, but more slowly than this, tending asymptotically to a maximum. The effect of temperature on the rate of decomposition is too small to be measured. An attempt is made to measure the effect of varying the intensity of the light by wrapping the tubes containing the solutions with different numbers of layers of thin paper. The results indicate that light of less than a certain intensity produces little or no reaction; above this intensity the rate of change is almost proportional to the intensity. The analogy between this result and the electrolysis of a solution with increasing *E.M.F.*'s is pointed out.

No indication of the existence of a photochemical extinction could be observed.

T. E.

**An Apparatus for the Measurement of Radioactivity.** BÉLA SZILARD (*Chem. Zeit.*, 1911, 35, 539—540).—A delicately suspended magnetic needle in metallic communication with a metal band, within which it lies at the zero position, is contained on an insulator inside a flat circular box with glass top etched with a circular transparent scale. The position of the needle is read by a lens in the axis of the needle support. By means of a side plunger a charge can be given to the needle and its metal band. It is adjusted to zero uncharged by rotating the whole instrument, and then charged. The rate of movement of the needle on its return to zero in presence of a radioactive substance is used to measure the activity. For work with emanations, the instrument is mounted on a cylinder bearing a central electrode in connexion with the needle.

F. S.

**The Presence of Helium in Autunites and the Period of Life of Ionium.** ARNALDO PIUTTI (*Le Radium*, 1911, 8, 204—205).—An examination of one of the specimens of Portuguese autunite investigated by Soddy (this vol., ii, 6) showed that the helium was largely present in the portion insoluble in hydrochloric acid. The spectrum of the gas from 3 grams of the original mineral containing 40% of autunite, obtained by calcining the mineral, was compared with that obtained by the calcination of 4.2 grams of the insoluble residue remaining after prolonged treatment with cold concentrated hydrochloric acid. The spectrum of helium was of similar intensity in the two specimens of gas. Since in dissolving the mineral in hydrochloric acid some of the helium in the insoluble residue may be evolved, calculations of the age of the autunite and of the life-period of ionium from this datum may be vitiated.

F. S.

**A Method of Making Visible the Paths of Ionising Particles through a Gas.** CHARLES T. R. WILSON (*Proc. Roy. Soc.*, 1911, A, 85, 285—288).—By using a suitable expansion apparatus the track

of individual  $\alpha$ - or  $\beta$ -rays, or of ionising rays of any kind, through a moist gas may be made visible by condensing water on the ions set free. The expansion chamber is cylindrical with flat, horizontal roof and floor, 7.5 cm. diameter, and between 4 and 5 mm. high before, and 6.2 mm. high after, expansion. The roof is coated below with a thin layer of clear gelatin, and the floor also with gelatin blackened by Indian ink, which prevents the deposition of dew on the chamber and forms an electrically conducting surface. Before expansion, a field of 16 volts per cm. acts to remove ions as fast as produced. The only ions "caught" on expansion are those produced within 0.025 second before expansion. For eye observation, a Nernst lamp and condensing lens, and for photography, a Leyden jar discharge through mercury vapour at atmospheric pressure (the mercury being boiled in a quartz tube) were employed, the spark being passed from 0.1 to 0.2 second after the expansion had taken place. The radium-tipped metal tongue of a spinthariscopes is placed inside the chamber, and the individual trails of the  $\alpha$ -rays are then clearly seen. Some of these show evidence of having divided into two trails, due to positive and negative ions under the influence of the field, prior to the moment of exposure. Those photographed before diffusion has had time to occur are remarkably sharply defined lines. With  $\beta$ -rays, absolutely straight thread-like lines are generally seen radiating from the source, while similar lines due to secondary or reflected  $\beta$ -rays cross the field in other directions. With  $\gamma$ -rays, the cloud is localised in streaks and patches, and consists mainly in fine straight thread-like lines traversing the chamber in all directions, due to the  $\beta$ -particles from the walls of the vessel. With  $X$ -rays, the cloudlets are mainly thread-like objects, varying in length from a few millimetres to a fraction of a millimetre, rarely straight, and many showing a peculiar beaded structure. The results are in agreement with Bragg's view that the whole of the ionisation by  $X$ -rays may be regarded as due to cathode-rays or  $\beta$ -rays arising from the  $X$ -rays. The question as to the form of the  $X$ -ray wave-front remains undecided. F. S.

**The Variation of Ionisation with Velocity for the  $\beta$ -Particles.** W. WILSON (*Proc. Roy. Soc.*, 1911, *A*, 85, 240—248).—Separate determinations (1) of the charge carried, (2) of the ionisation produced by the  $\beta$ -rays of radium *B* and *C*, separated by means of a magnetic field into bundles of rays of different velocities, have afforded data for the determination of the relative amount of ionisation produced by the individual  $\beta$ -particle at different velocities. The determination of the charge carried by the rays, and therefore the number of  $\beta$ -particles worked with, was made by allowing the rays, after being sorted out by the magnetic field, to enter a box, closed except for a small hole where the rays enter, and to measure the charge gained by the box in a vacuum by means of the deflexion of an attached gold-leaf system. To measure the ionisation, a box of exactly similar character was employed in the same place in the apparatus as ionisation chamber, the pressure of the air being between 0.1 to 5 cm. of mercury. The increase of ionisation due to multiple reflexion of

the rays from the walls of the box was separately determined and corrected for. As a result, it was found that the ionisation in free air per cm. of path produced by the  $\beta$ -particle varies inversely as the square of the velocity between velocities of 1.4 and 2.9 ( $\times 10^{-10}$  cm. per second). This result should follow if the same amount of energy is required for the production of each ion, since the average time spent by the  $\beta$ -particle within the atom is inversely proportional to the velocity, and the work done by the electron within the atom is proportional to the square of the time. In thick metal vessels, owing to the complicated manner in which the  $\beta$ -particles are scattered, no simple connexion exists, the ionisation  $I$  in a thick copper vessel being approximately represented by the equation:  $I = K(c - v)$ , where  $v$  is the velocity, and  $K$  and  $c$  are constants. F. S.

**Observation of  $\beta$ -Rays from Radium-D.** OTTO VON BAEYER, OTTO HAHN, and LISE MEITNER (*Physikal. Zeitsch.*, 1911, 12, 378—379).—A photograph of the magnetic spectrum of the  $\beta$ -rays of a product containing radium-D, -E and -F showed two groups of easily deviable  $\beta$ -rays due to radium-D. The velocity of these new rays is 0.37 and 0.31 (that of light = 1). These rays are therefore of the same order of velocity as the cathode rays. Only two of the members of radioactive series, actinium and mesothorium-1, remain in the disintegration, of which no rays have yet been observed. F. S.

**The  $\beta$ -Rays of the Active Deposit of Thorium.** OTTO VON BAEYER, OTTO HAHN, and LISE MEITNER (*Physikal. Zeitsch.*, 1911, 12, 273—279).—The photographic examination of the magnetic spectrum of the  $\beta$ -rays of the active deposit of thorium distinguishes three homogeneous groups of rays, that from thorium-A with velocity 0.63, and two very easily deviable groups with velocities 0.34 and 0.28 (velocity of light = 1). There is another feeble group of homogeneous rays of velocity 0.72. The  $\beta$ -rays of thorium-D are not homogeneous, and range in velocity from 0.93 to 0.95. These results, taken in conjunction with others, lead to the general conclusion that  $\beta$ -rays above 70—80% of the velocity of light are more or less heterogeneous, whilst  $\beta$ -rays of lower velocity are homogeneous. The slower  $\beta$ -rays in passage through matter suffer reduction of velocity without loss of homogeneity. Thus the two groups of velocity 0.63 and 0.72, after passage through 0.045 mm. of aluminium, had velocities 0.57 and 0.68. The faster  $\beta$ -rays through passage of 0.3 mm. of copper, and 0.1 mm. of platinum, did not experience a change of velocity of 1%. The degree of heterogeneity was not affected. The heterogeneity is probably impressed upon the beam in the immediate neighbourhood of the point of expulsion of the rays through a reflexion or secondary radiation effect. The former conclusion that the exponential law of absorption of  $\beta$ -rays indicates homogeneity is modified in consequence of these results. F. S.

**The Influence of Radium Rays on the Photo-electric Sensitiveness of Metals.** H. DEMMER (*Ber. Deut. physikal. Ges.*, 1911, 13, 313—327).—The influence of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -rays on the photo-electric activity of metals has been examined. With a copper plate

in a high vacuum, the photo-electric activity is unaltered when the plate is acted on by  $\alpha$ -,  $\beta$ -, and  $\gamma$ -rays. With a platinum plate in similar circumstances, the photo-electric activity increases under the influence of  $\alpha$ -rays, but this is due to the secondary effect, which consists in the removal of the adsorbed gases when the surface of the plate is bombarded by the  $\alpha$ -particles. In air at atmospheric pressure the phenomena of photo-electric fatigue, first observed by Crowther, are exhibited, but this is shown to be due to the ozone which is generated by the acting rays, and not to an action of the rays on the metal itself.

H. M. D.

#### The Production of Characteristic Röntgen Radiations.

R. WHIDDINGTON (*Proc. Camb. Phil. Soc.*, 1911, 16, 150—154\*).—When an element is acted on by primary Röntgen radiation of sufficiently high penetrating power, it emits a characteristic secondary radiation. In order to determine the nature of the primary radiation which is just sufficiently penetrating to cause an element to emit its characteristic secondary rays, the author has made experiments with cathode rays of different velocities. The critical velocities, which correspond with the commencement of the emission of the characteristic rays, were found to be as follows: aluminium 2.8, chromium 5.1, iron 5.7, nickel 6.1, copper 6.18, zinc 6.24, selenium  $7.25 \times 10^9$  cm. per second. These numbers show clearly that the critical velocity is nearly proportional to the atomic weight of the emitting element.

It has also been found that the energy of the Röntgen radiation for cathode rays of given velocity is proportional to the magnitude of the cathode ray current.

H. M. D.

#### The Intensity of Secondary Homogeneous Röntgen Radiation from Compounds.

J. CROSBY CHAPMAN and E. D. GUNN (*Proc. Camb. Phil. Soc.*, 1911, 16, 136—141).—Measurements have been made of the characteristic secondary Röntgen radiation which is emitted by strontium in the form of chloride and sulphate, and by tin as free metal and in the form of the nitrate. Standardised rays from an X-ray bulb were allowed to fall on a thin sheet of the metal or compound under investigation, and the secondary radiation measured by means of a Wilson tilted electroscope. The experimental data show that the intensity of the characteristic secondary radiation is solely dependent on the quantity of the emitting element present, and is therefore a purely atomic phenomenon. This result supports the view that the characteristic secondary radiation does not result from the subsequent bombardment of atoms by ejected electrons, for, if this were so, the intensities of the radiation from a metal and its compounds could not be equal.

H. M. D.

The Doppler Effect of Hydrogen Canal Rays. JOHANNES STARK (*Ber. Deut. physikal. Ges.*, 1911, 13, 353—356).—The interpretation of observations on the Doppler effect exhibited by canal rays in hydrogen by Gehrcke and Reichenheim (this vol., ii, 166) is said to be inconsistent with experimental results obtained by other authors.

H. M. D.

\* and *Proc. Roy. Soc.*, 1911, A, 85, 323—332.

**The Action of Cathode Rays on Certain Minerals, and the Nature of the Mineral Colorations.** CORNELIO DOELTER (*Monatsh.*, 1911, 32, 299—318).—The colour changes produced by the action of cathode rays and in some cases of ultra-violet rays on rock salt, sylvine, corundum, zircon, ruby, topaz, kunzite, barytes, and celestine, have been examined. In the case of rock salt, the behaviour of the naturally-coloured blue mineral was compared with that of rock salt coloured artificially by means of sodium and that coloured by the action of cathode rays. The three forms exhibit considerable differences in regard to the effect of high temperature and of ultra-violet light on the coloration.

As yet no satisfactory explanation of the colour changes can be given.  
H. M. D.

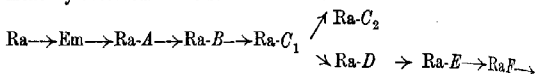
**The Behaviour of Radium Emanation at Low Temperatures.** R. W. BOYLE (*Phil. Mag.*, 1911, [vi], 21, 722—732).—The volatility of radium emanation at low temperatures ( $-130^{\circ}$  to  $-180^{\circ}$ ) has been investigated by a new method, in which the emanation was contained in a bayonet-shaped tube drawn out to a fine tip at one end, where the emanation could be condensed, and closed at the other end with a very thin mica window, thin enough to allow  $\alpha$ -rays to pass through. In this way the  $\alpha$ -rays escaping from the window furnish a measure of the amount of emanation in the vapour phase, the  $\alpha$ -rays from the condensed emanation not being able to impinge upon the window. The tip of the tube was cooled in pentane, surrounded with liquid air, which slowly evaporated, allowing the temperature to rise gradually while the ionisation produced by the  $\alpha$ -rays was observed. With large quantities of emanation and insensitive measuring apparatus, volatilisation appeared to take place sharply at about  $-160^{\circ}$ , but with smaller quantities of emanation and more sensitive measuring instruments, the volatilisation appeared to commence earlier, in one case as low as  $-170^{\circ}$ . The volatilisation appears to be normal, and occurs to a varying extent over a wide range of temperature.  
F. S.

**Typical Cases of Secondary Emanations Produced by Uranium-X.** W. B. HUFF (*Ion*, 1910, 2, 360—367).—Schmidt has established that the intensity of  $\beta$ -rays set up in metals by the action of uranium-X follows the order of their atomic weights, and the author by direct methods of comparing secondary emanations has confirmed this result.  
F. M. G. M.

**The Complex Nature of Radium-C.** KASIMIR FAJANS (*Physikal. Zeitsch.*, 1911, 12, 369—378).—Recoil experiments with pure radium-C, deposited from the sulphuric acid solution of the active deposit from a large quantity of radium, on a nickel plate have established the view of Hahn and Meitner that radium-C is complex. The recoil product (radium- $C_2$ ) gives out  $\beta$ -rays only, within the experimental error of the same absorbability as the total  $\beta$ -radiation of the active deposit. The product radium- $C_2$  has a half-period of 1.38 minutes, its radioactive constant being  $0.084[\text{sec.}]^{-1}$ . Since the



$\alpha$ -radiation of the active deposit does not come from radium- $C_2$  or from its product, it must come from radium- $C_1$ ; but the amount of radium- $C_2$  recoiled from radium- $C_1$  is very small, and is much more than to be expected of a  $\beta$ -ray recoil than of an  $\alpha$ -ray recoil. The  $\beta$ -activity of the recoiled radium- $C_2$  is only 1/20,000th of that of the source. Experiments on the recoil of radium- $D$  from the same source showed that about 25% of the atoms of radium- $D$  formed are recoiled. It follows in consequence that radium- $D$  must be the direct product of radium- $C_1$ , and not of radium- $C_2$ , and that the production of radium- $C_2$  from radium- $C_1$  is the first case of a multiple disintegration experimentally observed. The series therefore runs:



It is suggested that radium- $C_2$  may be the parent of actinium. It is probable that only a small part of the  $\beta$ -rays of the active deposit are due to radium- $C_2$ . The question as to what radiations the two kinds of disintegration of radium- $C_1$  are accompanied by remains to be investigated. The recoiled radium- $C_2$  is always accompanied by a minute amount of radium- $C_1$ , which may be due to the volatility of the latter.

In an appendix [with WALTER MAKOWER] the phenomenon of the recoil of radium- $C_2$  in a high vacuum is investigated. No greater quantity of radium- $C_2$  was obtained, than at atmospheric pressure in an electric field, but the quantity of radium- $C_1$  was increased about fifty times.

F. S.

The Radioactivity of Some Igneous Rocks from Antarctic Regions. ARNOLD L. FLETCHER (*Phil. Mag.*, 1911, [vi], 21, 770—773).—The radium and thorium contents of 13 specimens of rock from the Antarctic region of S. Victoria Land have been determined. The richest was a Kenyt lava, coloured red by infiltration of geyser water, which contained  $4.02 \times 10^{-12}$  radium and  $1.84 \times 10^{-3}$  of thorium (grams per gram). Three other specimens contained above 2 and 1.3, two above 1.3 and 0.7, and the remainder below 1.0 and 0.5 respectively for the radium and thorium in the above units. Remarkable constancy occurred in both radium and thorium in specimens from the same locality, independently of the chemical or petrographical character of the rock, the ratio of the radium to the thorium being remarkably constant in all the specimens at about  $1.7 \times 10^{-7}$ . Tests to see whether the presence of thorium interfered with the method employed to estimate the radium gave negative results.

F. S.

The Association of Lead with Uranium in Rock-Minerals, and its Application to the Measurement of Geological Time. ARTHUR HOLMES (*Proc. Roy. Soc.*, 1911, A, 85, 248—256).—For minerals of the same age, the ratio of lead to uranium should be a constant if the lead originates from the uranium. By working on certain minerals, such as thorite, zircon, and certain apatites and sphene, which segregate within themselves on crystallisation a much

larger proportion of uranium than is contained in the magma, the amount of lead initially present may be neglected. If changes in the amounts of lead and uranium occur, due to external chemical agencies, it is improbable that the two elements will be equally affected, so that if constancy of ratio of these two elements is found, it may be assumed that the mineral has not undergone appreciable alteration. These considerations limit the investigation to fresh, stable, primary rock-minerals, and those from the Christiania district of Norway, a geologically depressed area of 4000 square miles separated on every side by faults from the surrounding Pre-Cambrian gneiss, have been selected, the minerals being a series of thorite-bearing nepheline-syenites, probably of lower Devonian age. The uranium was estimated by means of the radium emanation and the lead gravimetrically as sulphate, and also colorimetrically by Harcourt's method (*Trans.*, 1910, 97, 841), the amount of copper and bismuth being negligible. In seventeen minerals arranged in the order of uranium content, the Pb/U ratio of the first fifteen varied from 0.041 to 0.068. With few exceptions the ratio increased somewhat as the uranium decreased, possibly due to the lead initially present in the magma having a gradually increasing relative importance. For the last two minerals, nepheline and felspar, the amount of uranium was only 0.001 and 0.0006%, the Pb/U ratio being 0.4 and 0.5. The mean value taken for the age-estimation was  $Pb/U = 0.046$ , which gives the age as 370 million years. The analyses collected by Boltwood of the uranium and lead in minerals are discussed with reference to the probable ages of the minerals. Wherever the geological evidence is clear, it is in agreement with that derived from the Pb/U ratio. The ages indicated by the latter are as follow: Carboniferous 340; Devonian 370; Pre-carboniferous 410; Silurian or Ordovician 430; Pre-Cambrian, (a) Sweden 1025 and 1275; (b) U.S.A., 1310 and 1435; (c) Ceylon 1640; in millions of years.

F. S.

**The Emission of Negative Electrons by Heated Potassium and Sodium, and the Conductivity of the Vapours of These Metals.** KARL FREDENHAGEN (*Physikal. Zeitsch.*, 1911, 12, 398—408).—Measurements have been made of the electrical conductivity of the vapours of sodium and potassium heated in highly exhausted tubes. When the exhaustion of the tubes is sufficiently high, the galvanometer indications at gradually increasing voltages indicate the existence of saturation currents. This is more clearly marked in sodium than in potassium vapour. The magnitude of the saturation current increases with the temperature in accordance with the exponential formula deduced by Richardson.

By means of experiments with the superheated vapours, it has been found that the current is almost entirely due to the emission of electrons by the heated metals. If, in addition, the vapours have a specific conductivity, the magnitude of this at temperatures below 350° is so small as to elude detection.

H. M. D.

**Radiation of Rubidium.** ÉMILE HENRIOT (*Compt. rend.*, 1911, 52, 1384—1386. Compare *Abstr.*, 1910, ii, 678).—The radiation from rubidium is more intense, but less penetrating, than that from

potassium. The rays are almost homogeneous; their coefficient of absorption by paper diminishes as the thickness increases, and is given by the equation:  $K_p/K_0 = 0.90e^{-100\rho} + 0.10e^{-250\rho}$ , where  $K_p$  is the intensity of radiation traversing  $\rho$ , the weight of paper per square cm.

A close proportionality exists between the radiation and the proportion of rubidium in the salts of the metal.

W. O. W.

**The Velocity of the Ions of Alkali Salt Vapours in Flames.**  
HAROLD A. WILSON (*Phil. Mag.*, 1911, [vi], 21, 711—718).—The results of earlier experiments on the conductivity of flames containing vapours of salts of the alkali-metals indicate that the positive ions are atoms of the alkali-metals carrying single atomic charges, but this is difficult to reconcile with the fact that the velocities of these ions are the same for all the alkali-metals. The results are re-examined from the point of view that the alkali-metal atoms in the flames exist as ions for only a fraction of the time, the experimental values found for the velocities being then the true velocities multiplied by these fractions. These fractions, deduced from the experimental data, are found to vary from 0.21 for the lithium ion to 0.99 for the cesium ion, on the assumption that the fraction varies as the square root of the atomic weight. This assumption is found to be in approximate agreement with the experimental data.

F. S.

**Velocities of the Electrons Produced by Ultra-violet Light.**  
A. LL. HUGHES (*Proc. Camb. Phil. Soc.*, 1911, 16, 167—174).—The influence of the nature of the surface layer on the velocity of emission of electrons by metals when excited by ultra-violet light has been investigated. Experiments were made with nickel, copper, zinc, cadmium, and mercury, and the effect of using the metal as anode and cathode, of allowing the metal to remain in different gases, and of preparing metal surfaces by distillation in a vacuum, was examined.

The results obtained show that these various forms of treatment give rise to considerable differences in the velocity of emission of the electrons. The surfaces obtained by distillation in a liquid air vacuum are more likely to be free from surface films than those which have been treated by a discharge. In support of this view, it is found that the increased velocities obtained for the fresh surfaces are much more constant and remain steadier than the values obtained after discharge. With ordinary polished metal surfaces, the low values of emission appear to be due to the presence of a retarding surface film.

H. M. D.

**The Influence of Changes of Temperature and Pressure in Gases on the Movement of the Ions Shown by Ultra-violet Light.**  
ALOIS F. KOVARIK and C. ZAKRZEWSKI (*Ion*, 1910, 2, 289—314).—A description of the apparatus and methods employed in an investigation to determine the influence of temperature and pressure on the size of the negative ions in plates of metal in dry and wet air and in carbon dioxide.

The results indicated that the mobility of ions is greater in dry than in wet air, greater in air than in carbon dioxide, and independent of the nature of the metal. Down to pressures of 200 mm. the

product of the mobility and pressure remain constant; below 200 mm. the product increases as the pressure decreases, especially rapidly at very low pressures.

With rising temperatures, the mobility increases, and at very high temperatures is inversely proportional to the density of the gas. At liquefaction temperatures, the mobility is much less than would correspond with the density of the gas, so that here the assumption of larger molecular aggregates appears to be justified. F. M. G. M.

**The Question of Valency in Gaseous Ionisation.** R. A. MILLIKAN and HARVEY FLETCHER, (*Phil. Mag.*, 1911, [vi], 21, 753—770. Compare this vol., ii, 175).—Direct unmistakable evidence has been obtained that the act of ionisation of air molecules by both primary and secondary X-rays of widely varying degrees of hardness, and by  $\beta$ - and  $\gamma$ -rays, consists, under all conditions examined, uniformly in the detachment of a neutral molecule of one single elementary charge. The method employed was to measure by a cathetometer the velocity of an illuminated single drop of oil under the joint action of gravity, and an opposed electric field, when it was kept near the upper, negative, plate of a condenser, while a sheet of X-ray ionisation was produced parallel and near to the lower, positive, plate. The drop was first so charged that the action of gravity nearly balanced that of the field; the X-rays were applied until a sudden start indicated that an ion had been caught by the drop, when the X-rays were stopped, the velocity was measured, the X-rays again applied until there was another sudden change of velocity, and so on, the movement of the same drop being often observed for several hours. The whole of the observations, with a very few doubtful exceptions, which are probably due to the simultaneous arrival of two ions, indicate that the charge of the drop changes its value by single atomic charges. Under the conditions, all but a few per cent. of the "catches" are of positive ions, and the smallness of the number of catches of negative ions is regarded as conclusive evidence that the greater part of the ionisation of the gas by X-rays is due directly to the primary rays, and not to secondary X-rays generated from them. The evidence derived from the work of Townsend and others that the positive ions produced by X-rays, particularly soft secondary X-rays, are doubly charged, is reviewed. The present experiments differ from earlier ones in that the charge on the ion is not measured after the ion has been formed for a considerable time, but is the charge at the moment of formation. The atomic structure of electricity is beautifully demonstrated by these experiments. For a single drop, three or four totally different velocities, due to an increment of the positive charge by one, two, three, or sometimes four, atomic charges, are observed, and no intermediate velocities ever occur. The different velocities are so characteristic that they can be distinguished by the eye unaided by a watch or chronometer. F. S.

**A Special Case of Distribution of Ionisation in a Gas. Thin Superficial Layer Containing Ions of Both Signs.** MAURICE DE BROGLIE (*Compt. rend.*, 1911, 152, 1298—1299. Compare this vol., ii, 356).—The production of a thin layer of ions on

the surface of quinine sulphate in process of hydration is somewhat analogous to the phenomena observed when Röntgen rays impinge tangentially on a metallic plate, except that in the latter case only negative ions are produced, and the layer has an appreciable thickness owing to secondary radiations. The extreme tenuity of the layer over the quinine sulphate crystals is sufficient to account for the difficulty in arriving at saturation, since the electrical field acts by diminishing the initial re-combination of the ions.

W. O. W.

**Electric Dispersion of Water and Ethyl Alcohol for Very Short Waves.** H. MERZYNG (*Bull. Acad. Sci. Cracov*, 1911, 123—133).—The refraction of electric waves by water and ethyl alcohol has been measured for wave-lengths ranging from 3.5 to 4.5 cms. For these waves the refractive index is appreciably different from the value for infinitely long waves, and the measurements afford information therefore as to the form of the dispersion curve. In the case of water, it is found that the refractive index increases with the wave-length. Both liquids exhibit anomalous dispersion.

H. M. D.

**The Electrical and Optical Behaviour of the Chlorine Flame.** J. FRANCK and P. PRINGSHEIM (*Ber. Deut. physikal. Ges.*, 1911, 13, 328—334).—When the electrical conductivity of a hydrogen chlorine flame is measured between unsymmetrical electrodes, a unipolar effect is observed, which is of opposite character to that exhibited by hydrogen or coal gas flames burning in air. This difference in behaviour is found whether a continuous or an alternating current is sent through the flame. In a similar manner, the dependence of the polarity on the temperature of the electrodes in the chlorine flame is the reverse of that found in the hydrogen or coal gas flames. With two equal electrodes, the temperature of the cathode is the chief factor which determines the conductivity in the latter, whereas the anode temperature is of primary importance in the chlorine flame.

These observations indicate that the mobility of the positive ions in the chlorine flame is much greater than that of the negative ions. Free electrons are therefore absent, and this is no doubt due to the great affinity of the molecules of electro-negative gases for electrons.

The absence of the yellow colour of sodium when this is introduced into the chlorine flame is probably connected with the absence of electrons. If, however, an oscillatory spark discharge is passed through the flame containing a bead of sodium chloride, an intense D-line emission is at once obtained.

H. M. D.

**The Relation of the Electrical Conductivity of Some Silver Amalgams to Temperature.** ANTONIO REYES CALVO (*Ion*, 1910, 2, 409—410).—The author measured the electrical resistance of very dilute silver amalgams (up to 0.06% Ag) between the temperatures of 0° and 20°, and found that at all concentrations it was merely a function of temperature.

At constant temperatures the resistance decreased with the rise of

concentration, and yielded a curve which was concave to the concentration axis.

F. M. G. M.

**The Conductivity of a Cadmium Amalgam.** ANTONIO REYES CALVO (*Ion*, 1910, 2, 408—409).—The tabulated results of experiments on the conductivity of various cadmium amalgams measured at different temperatures. With more than 1% of cadmium present, conductivity increased with the temperature, first quickly, then more slowly, until a transition point was reached and it became rectilinear. Increased concentration raised the temperature of the transition point. For very dilute amalgams, the conductivity between 0° and 20° may be represented by quadratic equations.

F. M. G. M.

**Liquid Helium. C. The Change of Electric Resistance of Pure Metals at Very Low Temperatures. IV. The [Electrical] Resistance of Pure Mercury at Helium Temperatures.** H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 13, 1274—1276. Compare this vol., ii, 368, 487).—The electrical resistance of pure mercury at liquid helium temperatures has been measured by the aid of a helium cryostat. At 13.9° (absolute) the resistance is 0.034 of that of solid mercury at 273° (obtained by extrapolation); at 4.3° it is 0.0013, and at 3° it is less than 0.0001. This shows that the resistance of mercury, like that of gold, becomes zero at a temperature which is experimentally attainable and appreciably higher than the absolute zero. The observations agree with the behaviour predicted by the author on the basis of Planck's theory.

H. M. D.

**Electrical Resistance of Antimony Selenides.** HENRI PÉLABON (*Compt. rend.*, 1911, 152, 1302—1305. Compare Châtelier, *Abstr.*, 1906, ii, 550).—The specific resistance of mixtures of antimony and selenium increases with the proportion of selenium until this corresponds with the compound  $Sb_2Se_3$ . For mixtures containing less selenium than the compound  $Sb_2Se_3$ , the specific resistance increases regularly with the temperature, and, on cooling, diminishes to the same extent. With higher proportions of selenium, it reaches a maximum as the temperature is raised, and then diminishes until fusion. If the mixture is then cooled, the values for the resistance are much higher than the original numbers, and the maximum occurs at a lower temperature.

W. O. W.

**Electromotive Force Produced by the Flow of Copper Sulphate Solution through a Capillary Tube.** L. RIÉRY (*Compt. rend.*, 1911, 152, 1375—1376).—A difference of potential of about 0.3 volt is observed between the ends of a capillary tube when an aqueous solution containing 1% of crystallised copper sulphate passes through, under a pressure of 90 atmospheres. The difference is proportional to the pressure, and diminishes as the proportion of copper sulphate increases.

W. O. W.

The Temperature-coefficient of Concentration Cells, in which the Same Salt is Dissolved in Two Different Solvents. ARTHUR P. LAURIE (*Proc. Roy. Soc. Edin.*, 1911, **31**, 375—396. Compare Abstr., 1908, ii, 1007).—The *E.M.F.* of the cell:  $\text{Pt} | 0.025 \text{KI} + 0.0138 \text{I}_2$  in water  $| 0.025 \text{KI} + x \text{I}_2$  in alcohol  $| \text{Pt}$ , gradually changes from a positive value to a negative one as  $x$  varies from 0.043 to 0.345, both at  $14^\circ$  and  $25^\circ$ , current in the direction of transferring potassium iodides from alcohol to water being defined as positive. This is in accord with the theory of such cells, as developed by Luther (Abstr., 1896, ii, 461) and Abel (Abstr., 1906, ii, 722). The curves showing the relation between the *E.M.F.* and  $x$  are roughly logarithmic, with approximately the same temperature-coefficients. Similar results were obtained with cells in which the alcohol was replaced by nitrobenzene, and with alcohol-water cells with potassium iodide in solution and silver-silver iodide electrodes. Using Abel's results as a starting point, it is shown theoretically that there is a connexion between the latent heats of solution and the observed results, of the form  $E = \lambda' - \lambda + T.de/dt$ , where  $\lambda'$  and  $\lambda$  are the latent heats due to the solution of one gram-mol. of potassium iodide in water and alcohol respectively (calling heat absorbed positive),  $E$  is the *E.M.F.*, and  $de/dt$  is the temperature-coefficient.

Starting with the cell  $\text{Ag, AgI} | 0.001 \text{KI}$  in water  $| 0.001 \text{KI}$  in alcohol  $| \text{Ag, AgI}$ , the concentrations of the aqueous solutions were varied from 0.001 to 0.1 and the *E.M.F.*'s measured. As the concentration of the aqueous solution increases, the *E.M.F.* changes from positive to negative, and the results are in accordance with the equation  $E = RT(\log C \times x - \log C')$ , where  $x$  is a constant, and  $C$  and  $C'$  are the concentrations of the alcoholic and aqueous solutions respectively.

It is further shown that the condition of electrical equilibrium is the potassium iodide-water-alcohol cell is not when both solutions are saturated with the salt, but is when the strength of the water solution is such that diffusion produces no salt precipitation when it is in contact with alcohol saturated with potassium iodide. This equilibrium is reached when the strength of the water solution is about 2 mols. of potassium iodide per 1000 c.c. T. S. P.

Electrochemical Behaviour of Tin. FRITZ FOERSTER and J. YAMASAKI (*Zeitsch. Elektrochem.*, 1911, **17**, 361—374).—The following potentials, referred to the normal hydrogen electrode, are measured at  $18^\circ$ :

$\text{Sn} | 0.9 \text{ mol. SnCl}_2 \text{ per litre} = -0.188 \text{ volt}$ ;  $\text{Sn} | 0.49 \text{ mol. SnSO}_4 \text{ per litre} = -0.190 \text{ volt}$ ;  $\text{Sn} | 0.49 \text{ mol. SnCl}_2 \text{ in } N\text{-HCl} = -0.204 \text{ volt}$ ;  
 $\text{Pt} | 0.25 \text{ mol. Sn}^{II} + 0.25 \text{ mol. Sn}^{IV} \text{ in } N\text{-NH}_4\text{Cl} = +0.131 \text{ volt}$ ;  
 $\text{Pt} | 0.25 \text{ mol. Sn}^{II} + 0.25 \text{ mol. Sn}^{IV} \text{ in } 0.5N\text{-HCl} = +0.158 \text{ volt}$ ;  
 $\text{Pt} | 0.25 \text{ mol. Sn}^{II} + 0.25 \text{ mol. Sn}^{IV} \text{ in } 2N\text{-HCl} = +0.138 \text{ volt}$ .

The effect of adding ammonium chloride or sulphate to the stannous solutions is also studied. The results indicate that the stannous salt exist largely in the complex forms in aqueous solution. The stannous-stannic potentials only become constant after several hours; the

change is attributed to the diminution of the concentration of the stannic ions by hydrolysis; it hardly occurs in strongly acid solutions.

The electrolytic reduction of stannic to stannous chloride at platinised platinum cathodes is studied. At the ordinary temperature the change is a slow one, so that a comparatively small increase of current density changes the cathode potential so much that tin is deposited (in 2*N*-acid solutions) or hydrogen is evolved (in 6*N*-hydrochloric acid).

The retardation of the reduction disappears almost entirely at higher temperatures (50–75°), and it is diminished by increase of the concentration of the stannic chloride or of the hydrochloric acid in the solution. T. E.

**Thermodynamics of the Cell; Hg, HgCl, PbCl<sub>2</sub>, Pb.** ROBERT LUTHER (*Zeitsch. Elektrochem.*, 1911, 17, 293–294).—From measurements of the *E.M.F.* of the above cell, the heat of the reaction  $\text{Pb} + 2\text{HgCl} = \text{PbCl}_2 + 2\text{Hg}$ , is calculated to be +21900 cal., direct thermochemical measurements having given 20100 cal. T. E.

**Mercurous Perchlorate Voltameter.** FRANK C. MATHERS and ALBERT F. O. GERMANN (*Indiana University Studies*, 1910, 41–49).—An acid solution of mercurous perchlorate is made by electrolysing a strong solution of perchloric acid with a mercury anode and a small platinum cathode. Conductivity measurements show that a solution of perchloric acid containing 0.43 gram per c.c. has the best conductivity. The conductivity of solutions of mercurous perchlorate increases slowly with the concentration, but the addition of free acid increases it greatly. For the voltameter, a solution containing 0.642 gram of mercurous perchlorate, 0.2836 gram of perchloric acid, and 0.04 gram of sodium perchlorate per c.c. was used. Without the sodium salt, a part of the mercury is deposited in the form of a black powder. In the voltameter the anode consists of 20 or 30 grams of mercury supported by a layer of glass wool on the bottom of a Gooch crucible, which is suspended in the electrolyte. The mercury cathode is placed below the anode, and is contained in a capillary tube with marks upon it, so that after a determination the mercury deposited may be run off exactly and either weighed or measured. A number of comparisons with silver and copper voltameters show that the error does not exceed about  $\pm 0.4\%$ . T. E.

**The Dissociation of Amphoteric Electrolytes.** LEONOR FICHAELIS (*Biochem. Zeitsch.*, 1911, 33, 182–189).—If  $\rho$  be the proportion of undissociated molecules of an amphoteric electrolyte, then  $\rho = 1/(1 + k_a/[H^+] + k_b/[OH^-])$ , where  $k_a$  is the acid, and  $k_b$  the basic association constant. The form of the curve when the hydrogen ion concentration is plotted as abscissæ, and  $\rho$  as ordinates, will depend on the magnitude of the product  $k_a k_b$ , which is characteristic for any particular amphoteric substance. The maxima of these curves are the isoelectric points. The smaller  $k_a k_b$ , the higher is the maximum above the abscissæ. When it reaches  $10^{-14}$ , the maximum reaches 1 but is, the substance is entirely undissociated). In electrolytes of



smaller value, there is a broad zone of hydrogen ion concentrations in which the substance is not dissociated. This is the case with tyrosine, leucine, and arsenious acid. Substances where  $k_a \cdot k_b \gg 10^{-14}$  do not appear to be capable of existing. S. B. S.

**Alterations in the Concentration of the Solution of a Magnetisable Salt in a Non-Homogeneous Magnetic Field.** WOLDEMAR VOIGT [with STATTSCHU] (*Chem. Zentr.*, 1911, i, 862—863; from *Nachr. K. Ges. Wiss. Göttingen*, 1910, 545—553).—Theory demands that concentration differences should be brought about in the solution of a magnetic salt placed in a non-homogeneous magnetic field. If a solution of such a salt is placed in a containing vessel so that the concentration of the solution varies in the vertical direction, an almost horizontal beam of light is deviated through the angle  $\alpha$ , where  $\alpha = DK(n^2 - n_0^2)dH^2/4n^2\rho BT \cdot dz$ , and  $D$  is the thickness of the vessel,  $K$  the magnetisation number,  $n$  and  $n_0$  the refractive indices of the solution and solvent respectively,  $B$  the Boyle's constant for the solution, which is considered to obey the gas laws,  $T$  the absolute temperature,  $\rho$  the density of the dissolved salt,  $H$  the intensity of the magnetic field.

For a 20% solution of ferric chloride,  $\alpha$  was found to be  $3.5 \times 10^{-4}$ , whilst according to the above formula it should have been  $5 \times 10^{-4}$ . If the dissociation of the ferric chloride is taken into account a better agreement is obtained. T. S. P.

**The Thermo electric Effects (Thermo-electric Forces, Thomson Effect) and the Thermal Conductivity of Certain Elements and Compounds and the Experimental Examination of the Electron Theories.** JOHANN KOENIGSBERGER and J. WEISS (*Ann. Physik*, 1911, [iv], 35, 1—46).—The thermo-electric properties and the thermal conductivity of silicon, molybdenite, iron pyrites, magnetite, ilmenite, manganite, ferric oxide, and graphite have been investigated. A method of measuring the thermal changes corresponding with the Thomson effect is described, in which short rods of the material are employed instead of long wires. The thermo-electric differences of potential at  $50^\circ$  of the various substances in contact with copper vary from  $+770 \times 10^{-6}$  volt in the case of molybdenite to  $-700 \times 10^{-6}$  volt for impure silicon. The experimental data are discussed in detail in reference to various deductions from the theory of electrons. II. M. D.

**Kinetic Theory of Gases and Thermodynamics.** A. BETHOUD (*J. Chim. Phys.*, 1911, 9, 352—381).—Considered thermodynamically a gaseous system is in equilibrium when its entropy is at its maximum. By the kinetic hypothesis, if all the molecules were at the same temperature at any moment, they would immediately assume a variety of temperatures from zero to infinity. This process being accompanied by a decrease of entropy is impossible thermodynamically. To meet this difficulty, the author assumes that each group of molecules of any particular velocity behaves as a "temperature isomeric" and distributes itself uniformly throughout the

whole system as if it were chemically unlike all similar groups of different velocity or temperature. Using this hypothesis the law relating the mean temperature to the proportion of molecules comprised between any two given temperatures was deduced on the principle of maximum entropy with the additional assumption that a rise in the mean temperature is accompanied by a proportional rise in velocity of all the molecules in the system. The relation deduced is identical with that deduced from Maxwell's formula in the case of monatomic gases. With polyatomic gases Maxwell's formula and the thermodynamic reasoning are not in accord unless Maxwell's formula is modified by substituting for the exponent 3 (the heat capacity of a monatomic gas) the value  $C_v$  of the heat capacity of the gas considered.

The author holds that Maxwell did not take into account the participation of internal molecular energy in the redistribution of energy which follows each molecular collision. Hence Maxwell's formula only holds for monatomic gases which have no internal energy.

R. J. C.

Dynamics of a Gas in Motion According to the Theory of Relativity. FERENCZ JÜTTNER (*Ann. Physik*, 1911, 35, 145—161).—A mathematical paper in which the author deduces the thermodynamic functions of a monatomic gas in motion on the basis of the theory of relativity.

H. M. D.

Thermal Conductivity of Liquids. ROBERT GOLDSCHMIDT (*Physikal. Zeitsch.*, 1911, 12, 417—424).—The method of measurement employed is similar to that used by Schleiermacher (*Ann. Physik*, 1888, 34, 623) in the determination of the thermal conductivity of gases at low pressures. A platinum wire of 0.05 mm. diameter is stretched by means of a spring along the axis of a silver capillary tube, 2 mm. wide, which is in direct contact with a massive cylinder of brass which completely surrounds the capillary. This arrangement ensures constancy of the temperature of the silver capillary throughout its whole length. The brass cylinder is supported in a Dewar tube which contains the liquid under investigation. The liquid fills the capillary tube, the main object of which is to eliminate to a large extent the disturbances which would otherwise result from convection. The errors which occur from the heat exchanges at the ends of the heated platinum wire can be avoided by the use of a shorter compensating wire which is fitted up in an exactly similar manner.

A current of known strength is passed through the platinum wire until a stationary condition is reached. The resistance of the wire in this condition is measured, and from the current intensity and the wire resistance, the temperature of the wire and the thermal conductivity of the surrounding liquid can be calculated.

Measurements have been made for a number of organic liquids. From the data for the alcohols it appears that the conductivity decreases as the molecular weight increases and as the structure becomes more symmetrical. For pentane, measurements were made over

an interval of  $210^{\circ}$ , and for ethyl ether and toluene over  $94^{\circ}$ . In all cases the temperature-coefficient is negative, and varies from 0.2 to 1.5% per degree.

H. M. D.

**The Specific Heat of Water.** WILLIAM R. BOUSFIELD and W. ERIC BOUSFIELD (*Phil. Trans.*, 1911, A, 211, 199—251; *Proc. Roy. Soc.*, 1911, A, 85, 302—304).—The mechanical equivalent of heat has been determined in terms of the mean calorie from  $13^{\circ}$  to  $55^{\circ}$  by a continuous flow calorimetric method in which a current of water was passed through a Dewar vessel of three litres capacity containing an electric heater. The water entered at about  $13^{\circ}$  and left at about  $55^{\circ}$ . The heater consisted of a spiral glass tube of small bore, into the end of which were sealed platinum electrodes. The mercury in this tube is connected with a thermometer tube, so that the spiral forms a thermometer bulb. Such a mercury resistance is free from a "thermoid" effect exhibited by ordinary resistances when a large current is passed through them. When this effect is present, the electric resistance is not only dependent on the temperature, but also on the strength of the current. The passage of this appears to induce a state of strain which temporarily alters the resistance by an amount which may reach several hundredths of a per cent.

The continuous flow experiments gave  $J_{13}^{55} = 4.182$  for the value in joules of the mean calorie between  $13^{\circ}$  and  $55^{\circ}$ . By heating a known quantity of water in successive stages, the values of  $J_{13}^{15}$ ,  $J_{15}^{20}$ ,  $J_{20}^{25}$ , and  $J_{25}^{30}$  were obtained. From these data the value of  $J$  at any temperature  $\theta$  is found to be given by the equation:  $J = 4.2085 - 0.003022\theta + 0.00007833\theta^2 - 0.000000490\theta^3$ . This yields 4.179 as the joule equivalent of the  $15^{\circ}$  calorie, and indicates a maximum specific heat corresponding with 4.174 joules at about  $25^{\circ}$ .

H. M. D.

**Specific Heats of Solids at Low Temperatures.** HERMANN BARSCHALL (*Zeitsch. Elektrochem.*, 1911, 17, 341—345).—The substance is cooled to the temperature of liquid carbon dioxide and allowed to fall into liquid oxygen at its boiling point, the quantity of gas evolved is measured, and the specific heat calculated by means of the latent heat of evaporation of oxygen. The values of the specific heat between about  $-75^{\circ}$  and  $-183.3^{\circ}$  measured in this way are: Lead, 0.0294; silver, 0.0492; cadmium, 0.0503; sulphur, 0.116 to 0.121; mercury, 0.0316; bromine, 0.073; mercuric iodide, 0.0375; lead iodide, 0.0377; lead bromide, 0.0463.

T. E.

**The Atomic Heats of the Elements.** JOHANN KOENIGSBERGER (*Zeitsch. Elektrochem.*, 1911, 17, 289—293).—The effect of free electrons on the atomic heat is discussed. A free electron has the same atomic heat as the atom of a monatomic gas. In metals the electrons remain free even at very low temperatures, whilst in bad conductors of electricity they are mostly combined. It is pointed out that at low temperatures the atomic heats of bad conductors are much less than 3, whilst those of the metals are greater than 3. At high temperatures the atomic heat of a metal is made up of the part due to

the free electrons and that due to the motion of the atoms. The latter, according to Einstein's views, is about 6, whilst the former is 3 when the metal contains one free electron per atom; as a matter of fact, the atomic heats of many metals are nearly 9 at high temperatures.

T. E.

**Molecular Heat of Fusion.** ÉMILE BAUD' (*Compt. rend.*, 1911, 152, 1480—1483).—Traube has shown that the co-volume of a liquid expands as a gas, proportionally to  $T$ , the absolute temperature. The variation in molecular volume at the moment of solidification,  $\Delta_v$ , is the difference between the co-volume of the liquid,  $V$ , and the co-volume of the solid,  $V'$ , supposing that the atoms of liquid and solid occupy the same volume. At constant temperature,  $t$ , it follows that:  $\Delta_v = (V - V') \cdot T / (273 + t)$ . Substituting this expression in Clapeyron's equation and integrating, this gives  $p = Q/T \cdot (273 + t) / (V - V')$ , where  $Q$  is the molecular heat of fusion. At constant pressure  $Q/T = k(V - V')$ , or, since  $V - V'$  is proportional to  $T$ ,  $Q = k(V - V')^2$ . The molecular heat of fusion of a substance should then be proportional to the variation in volume at the temperature of fusion. This conclusion has been found to agree with recorded observations in the case of ethylene dibromide, the three xylenes, naphthalene, and antimony trichloride.

W. O. W.

**Gaseous Mixtures. Freezing-point Curves of Gaseous Systems.** GEORGES BAUME (*J. Chim. Phys.*, 1911, 9, 245—289).—An apparatus has been constructed for the purpose of obtaining the liquidus curves of gaseous mixtures. The mixtures are synthesised volumetrically.

Successive litres of gas at  $0^\circ$  and a known pressure, which may be less than 760 mm., if necessary, are distilled into the cryoscopic tube, which is cooled in liquid air. The gravimetric composition of the mixtures is estimated from the densities of the gases, all the usual corrections being applied. The cryoscopic tube is provided with a magnetically operated platinum stirrer and an isopentane thermometer.

The error in the estimation of the masses is probably 1 in 3000, but is certainly not more than 1%. The temperatures are accurate to about  $0.25^\circ$ .

The liquidus curve of the system methyl ether-hydrogen chloride was determined. Hydrogen chloride melted at  $-111.4^\circ$  and methyl ether at  $-138.5^\circ$ . The curve exhibits two maxima at  $-97.1^\circ$  and  $-102.8^\circ$ , the mixtures having the compositions  $\text{Me}_2\text{O} \cdot \text{HCl}$  and  $\text{Me}_2\text{O} \cdot 4\text{HCl}$  respectively. Between these maxima, mixtures containing 27 to 38% of molecules of methyl ether are highly viscous, giving vitreous solids, so that the curve cannot be determined.

Extrapolation suggests an eutectic at about 30% of molecules of ether, but if the high viscosity indicates a third molecular compound there would be three maxima and four eutectic points in the complete liquidus curve.

R. J. C.

**The Depression of the Freezing Points of Sodium and Calcium Chlorides.** FRANCIS E. E. LAMPLOUGH (*Proc. Camb. Phil. Soc.*, 1911, 16, 193—196).—The following values were obtained for

the molar depression of the freezing point of calcium chloride, strontium chloride, 240; lithium chloride, 340; sodium chloride, 362; barium chloride, 380; potassium chloride, 448. From the depression of the freezing point of sodium chloride, the calculated molecular lowerings are: sodium bromide, 81; potassium chloride, 166; lithium chloride, 164; calcium chloride, 180; strontium chloride, 176; barium chloride, 202; sodium carbonate, 180; sodium sulphate, 204.

A complete series of freezing-point measurements for the binary system, sodium and calcium chlorides, was also made. The freezing-point diagram is of the simplest type, and exhibits a eutectic corresponding with about 50 mols. % of the two chlorides and about 495°. It is probable that the components separate out in the pure condition from all fused mixtures.

H. M. D.

**Heat of Evaporation of Oxygen.** HERMANN BARSCHALL (*Zeitsch. Elektrochem.*, 1911, 17, 345—348).—A known quantity of heat was added electrically to liquid oxygen at its boiling point, and the quantity of gas evolved was measured. Full details of the precautions taken to avoid error are given. The results of six experiments gave values lying between 51.23 and 51.38, mean 51.3 calories per gram at 763 mm. pressure.

T. E.

**Influence of Water Vapour on Measurements in a McLeod Gauge.** MARCEL GUICHARD (*Bull. Soc. chim.*, 1911, [iv], 9, 435—438).—Aqueous vapour behaves like a gas when its tension is low, so that its pressure in a McLeod gauge is given by the ordinary formula  $h = a/v/V - v$ , where  $h$  is the initial pressure at volume  $V$ , and  $a$  the increase in pressure necessary to reduce  $V$  to  $v$ . When the tension of aqueous vapour is high, then under compression the vapour attains its maximum tension,  $f$ , for the temperature of the surrounding atmosphere, and under these conditions  $a = f - h$ . Further,  $a$  reaches its maximum when  $h = fv/V$ , and decreases again for higher values of  $h$ . Consequently, when the tension of aqueous vapour in an apparatus rises from nil to its value at saturation point, the values of  $a$  read on the gauge increase to a maximum where  $h = fv/V$  and then diminish, so that every value of  $a$  corresponds with two initial tensions. Experimental data confirming these conclusions are given.

T. A. H.

**Optical Method of Measuring Vapour Pressures: Vapour Pressure and Apparent Superheating of Solid Bromine.** CLIVE CUTHBERTSON and MAUDE CUTHBERTSON (*Proc. Roy. Soc.*, 1911, A, 85, 306—308).—The refractivity of bromine vapour has been measured by means of Jamin's interferometer, the refractometer tube of the instrument being in communication with a reservoir containing solid bromine at a definite temperature. The temperature of the cooling bath was slowly raised, and the number of interference bands crossing the field of view was counted. Assuming that the refractivity and the pressure are proportional to the density of the vapour, the refractometric observations can be used for the calculation of the vapour pressure at any temperature if the vapour pressure for one particular temperature is known. The calculated pressures can be

represented by means of the equation  $p = a \cdot b^x$ , in which  $a = 2.485 \times 10^{-8}$  and  $b = 1.0834$ .

With slowly rising or falling temperature, irregularities are observed at the melting point, which seem to show that superheating and super-cooling take place.

H. M. D.

**Binary Liquid Solutions.** C. MARILLER (*Bull. Assoc. chim. Sucri. Dist.*, 1911, 28, 774—776).—The depression of the vapour pressure of ethyl ether by the addition of foreign substances can be satisfactorily expressed by the equation  $100/f' = 1 - KN$ , in which  $f$  is the vapour pressure of ether,  $f'$  that of a solution which contains  $N$ -gram-molecules of the dissolved substance in 100 of the binary mixture, and  $K$  is a constant, approximately equal to unity, which is approximately independent of the nature of the dissolved substance.

H. M. D.

**Hydrofluorides of Alkali Fluorides.** ROBERT DE FORCRAND (*Compt. rend.*, 1911, 152, 1556—1559. Compare this vol., ii, 488).—A review of salts of the type  $MF \cdot HF$  from the thermochemical point of view. The following numbers express in Calories the heat of fixation of a molecule of solid hydrogen fluoride on a molecule of solid alkali fluoride:  $NaF + 8.3$ ,  $KF + 12.76$ ,  $RbF + 13.78$ ,  $CsF + 14.77$ . It will be seen that, as in the case of the heats of dissolution of the normal salts studied previously, the sodium salt stands somewhat apart from the rest of the series. Although the stability of the normal fluorides increases in the order given above, the contrary is found to be the case with the hydrofluorides.

Rubidium and caesium fluorides are capable of absorbing excess of hydrogen fluoride to form compounds containing  $2HF$  and  $3HF$ .

W. O. W.

**Derivatives of Styrene; Rectification of Some Experimental Errors.** PAUL LEMOULT (*Compt. rend.*, 1911, 152, 1402—1404).—The author has determined the heats of combustion of styrene and a number of its derivatives, and has obtained the following values (expressed in Calories), the first three of which differ considerably from those given by Auwers, Roth, and Eisenlohr (*Abstr.*, 1910, ii, 586). Styrene, 1059.1,  $\alpha$ -methylstyrene, 1217.3;  $\alpha\beta$ -dimethylstyrene, 2510.3, di- $p$ -methoxystilbene, 2018. These numbers agree with the theoretical values calculated on the assumption that the hydrocarbons are unsaturated compounds, whereas those obtained by Auwers, Roth, and Eisenlohr are abnormal and correspond more closely with saturated compounds. The increase in the heat of combustion when freshly distilled styrene is kept for a few hours, referred to by these authors, could not be confirmed.

W. O. W.

**The Value of the Critical Quantities.** JOHANNES D. VAN DER WAALS (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 13, 1211—1231).—A theoretical paper in which the author discusses the variation of the term  $b$  in van der Waals' equation with the total volume occupied by the substance.

H. M. D.

The Value of the Volumes of the Co-existing Phases of a Simple Substance. JOHANNES D. VAN DER WAALS (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 13, 1253—1262).—The deviations exhibited by saturated vapours from the requirements of the van der Waals' equation are discussed in reference to the phenomenon of quasi-association.

H. M. D.

Weight of a Falling Drop and the Laws of Tate. IV. Standardisation of a Tip, and the Calculation of the Surface Tension and Molecular Weight of a Liquid from the Weight of its Falling Drop. J. LIVINGSTON R. MORGAN (*J. Amer. Chem. Soc.*, 1911, 33, 643—657).—In the earlier papers (Abstr., 1908, ii, 356, 668; this vol., ii, 372) the standardisation of the tip of the capillary tube, that is, the determination of the normal molecular temperature-coefficient,  $k$ , of all non-associated liquids falling from it, was effected by means of Ramsay and Shields' formula, connecting surface-tension with capillary rise. It is now shown that by this method the experimental error is multiplied to such an extent as to render the results misleading, and a new method has therefore been adopted which is based solely on the equation  $w(M/d) = k(t_c - t - 6)$ . The surface-tension in dynes of any liquid at any temperature can be calculated by multiplying its drop weight in mg. from the tip at that temperature by the ratio of the  $k$  value of surface-tension to the  $k$  value for the tip, both being found by the use of benzene ( $t_c = 288.3^\circ$ ) as the standard. Any liquid, which, with the normal (benzene) value of  $k$  ( $k_n$ ), gives the same calculated value of  $t_c$  at all temperatures of observation must be regarded as a normal non-associated liquid, since this proves that the normal  $k$  is also the correct change per degree of its molecular function. The calculated value,  $t_c$ , need not always agree with the observed value of the critical temperature, and this indicates that whilst some liquids are in corresponding states when equally removed from their critical temperatures, others are only so when equally removed from another, fictitious, temperature.

Aniline, pyridine, and quinoline are shown from this point of view to be perfectly normal in molecular weight.

The application to drop weight of the empirical formula for calculating  $t_c$  without a knowledge of the molecular weight as given by Walden (this vol., ii, 97) leads to results which differ but little from those calculated by means of  $k_n$ .

E. G.

Weight of a Falling Drop and the Laws of Tate. V. Drop Weights of Fifteen Non-associated Liquids as Found by the Use of the New Form of Apparatus, and the Molecular Weights Calculated for Them. J. LIVINGSTON R. MORGAN and EDGAR G. THOMSEN (*J. Amer. Chem. Soc.*, 1911, 33, 657—672).—It is shown, according to the new definition of molecular weight (preceding abstract), that is, that the constant  $k_n$  gives for the liquid a constant value of  $t_c$  independent of the temperature of observation,  $t$ , in the relation  $w(M/d)^{\frac{1}{2}} = k_n(t_c - t - 6)$ , that ether, ethyl butyrate, anisole, phenetole, ethylene dibromide, chloroform, benzonitrile, and carbon disulphide must be regarded as non-associated. The same

conclusion can be reached from the results of capillary rise. The calculated values of  $t_c$  agree closely with the observed critical temperatures in the cases of ether and chloroform, but the fictitious values of the critical temperatures found for the other liquids agree with those calculated from the capillary rise. The values of  $t_c$ , both true and fictitious, found by the modified Walden method without the use of the molecular weight, agree as closely as could be expected. The calculated value,  $t_c$ , for a mixture of equal weights of benzene and carbon tetrachloride is the mean of the values found for the two liquids separately.

E. G.

**Weight of a Falling Drop and the Laws of Tate.** VI. Drop Weights of Twenty New Non-Associated Liquids and the Molecular Weights Calculated for Them. J. LIVINGSTON R. MORGAN and G. K. DAGHLIAN (*J. Amer. Chem. Soc.*, 1911, 33, 672—684).—It is shown, by using the new criterion of normal molecular weight (preceding abstracts), that the following liquids are as completely non-dissociated as benzene: bromobenzene, bromine, ethylidene chloride, toluene, phosphorus trichloride, *o*-, *m*-, and *p*-xylenes, mesitylene, ethylbenzene, iodobenzene, fluorobenzene, cymene, ethylene dichloride, methylaniline, ethylaniline, isobutyl acetate, carbon disulphide, and diphenylmethane. In the case of dimethylaniline, a somewhat abnormal value was obtained for the molecular weight, but this was probably due to partial decomposition of the substance.

The calculated values of  $t_c$  agree closely with the observed values of the critical temperature in the cases of bromobenzene, bromine, ethylidene chloride, toluene, phosphorus trichloride, and *o*-, *m*-, and *p*-xylenes, whilst the difference between the calculated and observed values is less than 1% for mesitylene and but little greater for ethylbenzene and iodobenzene. The calculated values of  $t_c$  from drop weight determinations agree well with those obtained from capillary rise in the case of eleven liquids which have been studied by the latter method, but the mean values from capillary rise for mesitylene and *m*-xylene do not accord with those calculated from the drop weight.

The values of  $t_c$ , calculated by the Walden method without the aid of molecular weight, agree well in only eight cases, out of sixteen to which it could be applied, with those calculated from  $k_D$ , and it therefore seems that the relation is probably not so general as was at first supposed.

E. G.

**Apparatus for Determination of Viscosities, Especially of Serum and Other Animal Fluids.** LEO VON LIEBERMANN (*Biochem. Zeitsch.*, 1911, 33, 218—221).—An apparatus is figured, in which a gilded disk is allowed to vibrate in the liquid under investigation, and the time and amplitude of the vibrations are determined by means of reflexion of a beam of light on to a scale from a mirror attached to the wire suspending the disk. The comparative viscosities of two liquids can be calculated from the formula:

$$\eta_1/\eta_2 = d_2/d_1 \cdot T_2/T_1 \cdot (\lambda_1 - \lambda_0/\lambda_2 - \lambda_0)^2,$$

where  $\eta_1$ ,  $\eta_2$  are the viscosities,  $d_2$ ,  $d_1$  the specific gravities,  $T_2$ ,  $T_1$



the times,  $\lambda_2$ ,  $\lambda_1$  the logarithmic decrements of the amplitudes, and  $\lambda_0$  the logarithmic decrement of the amplitude in air. The advantages and disadvantages of the method as applied to serum are described.

S. B. S.

**Viscosity of Cellulose Nitrate Solutions.** C. PRIEST (*Zeitsch. angew. Chem.*, 1911, 24, 968—972. Compare Abstr., 1910, i, 464).—An account of an investigation on the viscosity of solutions of cellulose nitrates. The viscosities were measured by (1) Engler's apparatus, (2) Cochiu's viscometer, and (3) a viscometer, similar to that of Cochiu, in which the time taken by a hollow, glass bulb to rise through a given depth of liquid is measured. A description and sketch of this new form of viscometer is given.

It is found that the ratios of the viscosities determined by the three methods vary with different solutions; in other words, the viscosities obtained by the three methods cannot be compared with one another.

The viscosity of a solution of cellulose nitrate is dependent on (1) the presence of impurities, such as acetic acid, aldehyde, etc., (2) the duration and temperature of nitration of the cellulose, and (3) the presence of oxycelluloses and hydrocelluloses in the cellulose employed. All these factors produce a marked reduction of viscosity. Solutions of gun-cotton and collodion-wool also become less viscous when kept, although the change takes place very slowly.

It is the author's opinion that the viscosity of a colloidal cellulose nitrate solution is not determined by the magnitude of the cellulose nitrate molecule, but rather by the nature and size of the colloidal particle.

W. H. G.

**Viscosity of Emulsions** BANCELIN (*Compt. rend.*, 1911, 152, 1382—1383. Compare Perrin, this vol., ii, 480).—The viscosity  $K'$  of an emulsion of mastic is found to agree with the equation  $K' = K(1 + 2.9\phi)$ , when  $K$  is the viscosity of the liquid containing in suspension solid spheres, of total volume  $\phi$ , in unit volume of emulsion. Einstein (*Ann. Physik*, 1906, [iv], 19, 289) on theoretical grounds deduced the expression  $K' = K(1 + \phi)$ , but has now altered this to  $K' = K(1 + 2.5\phi)$  (private communication). The viscosity of sucrose and glycerol solutions is represented by an analogous formula, but carbamide and metallic salts show smaller coefficients of viscosity. Extrapolation from the first formula and from that expressing the coefficient of diffusion of an emulsion gives the value  $70 \times 10^{12}$  for  $N$ , the number of molecules in a gram-molecule.

W. O. W.

**Dissociation of the Compound  $\text{ThCl}_4 \cdot 18\text{NH}_3$ .** EDOUARD CHAUVENET (*Ann. Chim. Phys.*, 1911, [viii], 23, 275—280. Compare Abstr., 1910, ii, 872).—Dry ammonia gas was passed through a tube reaching to the bottom of a small distillation flask containing anhydrous thorium chloride, a long manometer tube containing a mercury index being sealed to the side-tube. The air being displaced, the flask was immersed in acetone and snow until a quantity of liquid ammonia had accumulated. The excess was then evaporated by placing the flask in

liquid methyl chloride. The (previously constricted) neck was then sealed off, at the same time the necessary mercury being poured into the gauge. Four observations of the dissociation pressure between 250° and 281° abs. were made, the results being plotted on a curve against the absolute temperatures.

From the difference between the heats of formation of  $\text{ThCl}_4 \cdot 18\text{NH}_3$  and  $\text{ThCl}_4 \cdot 12\text{NH}_3$  previously determined by the author, the heat of fixation of  $6\text{NH}_3$  on the latter has been found to be 8.83 cal. per mol.  $\text{NH}_3$ . Dividing this quantity ( $Q$ ) by the absolute temperature at which the dissociation pressure equals 760 mm. (determined from the above-mentioned curve) gives practically the same value of  $Q/T$  as that found by Matignon (Abstr., 1899, ii, 273) with other ammoniacal metallic chlorides. Moreover, substitution for  $p$  of the observed value of the dissociation pressure at 281° abs. in the reduced form of Clapeyron's formula:  $Q = 2/1000.273T/T - 273.\log.p/p_0$  ( $p_0$  being the dissociation pressure at 273° abs.;  $T = 281$ ) gives a value for  $Q$  closely agreeing with that observed.

J. D. K.

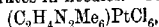
**Capillary Rise of Amines, Phenols, and Aromatic Hydroxy-Acids.** ZDENKO H. SKRAUP and ERNST PHILIPPI (*Monatsh.*, 1911, 32, 353—372. Compare Abstr., 1909, ii, 868; 1910, ii, 191, 934; this vol., ii, 21).—The capillary rise of weak hydroxides is smaller than that of strong. One purpose of the present paper is to ascertain whether the abnormal rise of ammonia and ethylamine, which is greater than that of the strongest alkali hydroxides, is exceptional or is characteristic of all amines. It is found in the case of aqueous ammonia (and of some amines) that the rise is very different according as the indicating strip is used without any enclosure or is suspended in a tube closed at its upper end and adjusted almost to the level of the basin containing the solution under examination. All the experiments, therefore, have been conducted under the latter conditions. The results are as follows: Aqueous ammonia shows a rise which diminishes with decreasing concentration. Hydroxylamine and hydrazine exhibit rises considerably greater than those of the strong alkali hydroxides. At equivalent concentrations, methylamine, ethylamine, and amylamine show almost identical rises; the same is true of the corresponding quaternary bases, the rise being somewhat smaller. Methylamine and dimethylamine exhibit the same rise, which is considerably higher than that of potassium hydroxide at the same concentration; trimethylamine, like ammonia, gives very different rises according to whether the strip is enclosed or not. Ethylenediamine, tetramethylethylenediamine, and hexamethylethylenediammonium hydroxide exhibit rises only slightly smaller than those of the corresponding monoamines at the same concentrations. In the case of aromatic mono- and di-amines the regularities are not so pronounced as the preceding, but here again the monoamines (aniline and the toluidines) exhibit greater rises than the diamines (the phenylenediamines, *m*-tolylene-diamine, 1:8- and 1:5-naphthylenediamines); in all cases, except the naphthylenediamines, the rises are much greater than those of potassium hydroxide at the same concentration. The position of the amino-group affects the rise; thus of the

toluidines the ortho-compound shows the greatest rise, whilst in the case of the phenylenediamines the ortho- and the meta-isomerides exhibit equal rises, that of the para-compound being considerably smaller. The hydrochlorides of some aromatic amines have been examined. The rise, tested by a colour reaction for the base, is the same for the salt as for the free amine, but the height of the acid zone is considerably smaller.

Some phenols and aromatic hydroxy-acids have been examined under the preceding conditions. The diminution in the rise with decreasing concentration is very much slower with phenols than with amines. Phenol, catechol, and quinol exhibit approximately equal rises, those of resorcinol, pyrogallol, and phloroglucinol being somewhat smaller.

Salicylic, *p*-hydroxybenzoic, protocatechuic, and gallic acids have also been examined. When tested by ferric chloride paper the rise almost equals that of the wet zone (100 mm.), and consists of an upper faint zone and a lower strong zone, a behaviour due to the ash in the paper which forms salts with the acid; it has been shown previously that salts are very slightly adsorbed. The acid zone is very much lower and decreases rapidly with increasing dilution.

Hexamethylethylenediammonium iodide,  $C_6H_{18}(NMe_2I)_2$ , decomp.  $250^\circ$ , is obtained by treating ethylenediamine in methyl alcohol with methyl iodide (2 mols.) and then with potassium hydroxide in methyl alcohol, repeating these two operations on the liberated base, and finally adding a third portion (2 mols.) of methyl iodide, whereby the diammonium iodide separates in needles. The *platinichloride*,



is described. Tetramethylethylenediamine is obtained by distilling an aqueous solution of hexamethylethylenediammonium hydroxide; its *platinichloride* crystallises in orange-red plates. C. S.

**Historical Data Relating to Osmotic Force.** Rectification of Authors' Names. AUGUSTE ROSENSTIEHL (*Compt. rend.*, 1911, 152, 1305—1308).—This note relates to the origin of the theory that the phenomena of dissolution are analogous to those of the vaporisation of substances. W. O. W.

**Osmotic Pressure of Colloids.** JACQUES DUCLAUX and Mme. E. WOLLMAN (*Compt. rend.*, 1911, 152, 1580—1583. Compare Baylis, *Kolloid Zeit.*, 1910, 8, 23).—The osmotic pressure of a colloidal solution of cellulose nitrate in acetone has been measured at different concentrations, using a semi-permeable membrane of denitrated collodion. The ratio of the pressure to concentration, which should be constant if the solution obeyed the ordinary laws, varies markedly, even at low concentrations. The ratio, which is 0.53 in a 0.11% solution, becomes 6.83 for a 1.41% solution. Application of van der Waals' equation for compressed gases does not bring the results into concordance.

It would seem, therefore, that the abnormal osmotic pressures of colloids must be regarded as depending on the peculiar nature of the colloid molecule. W. O. W.

**Rate of Dissolution in Gas-Liquid Systems.** TOR CARLSON (*J. Chim. Phys.*, 1911, 8, 228—244 \*).—The velocity with which a gas dissolves in a liquid at rest depends on the rate of diffusion of the gas into the bulk of the liquid from the saturated surface. According to Fick's law the rate of diffusion is proportional to the concentration gradient in the layer of solution considered.

Hence if  $c$  is the concentration of gas dissolved at any time  $t$ , and  $S$  be the concentration at saturation,  $dc/dt = K(S - c)$ , where  $K$  is a constant depending on the diffusion coefficient,  $D$ , at the given temperature and the area,  $a$ , and thickness of the saturation layer. This leads to a logarithmic dissolution law similar in form to the unimolecular reaction law. When the liquid is stirred at  $n$  revolutions per minute, the saturation layer is diminished in thickness proportionally to  $1/\sqrt{n}$ , just as Brunner found when dissolving benzoic acid in water; hence  $K = K'n^1/2Da$ . The constant  $K'$  is characteristic of the apparatus employed. The author has measured the velocity of dissolution of oxygen and of carbon dioxide in water, estimating the former by Winkler's iodine method, and the latter by Pettenkofer's baryta method. The unimolecular law is found to hold in both cases. The ratio of the diffusion constants,  $D_{O_2} : D_{CO_2} = 1.158$ , determined from the rates of dissolution under similar conditions approximates to the ratio determined by diffusion measurements, namely, 1.166. The concordance lends support to the above theoretical views.

With oxygen and carbon dioxide, the rates of dissolution and liberation from water are practically the same, the latter being sometimes 3—4% higher. The amount dissolved in a given time is proportional to the partial pressure of the gas, but the velocity constant is independent of pressure.

The Arrhenius exponential law appears to hold for the effect of temperature on the rate of dissolution, but no theoretical conclusion is drawn from this.

R. J. C.

**Possible Solid Solution of Water in Crystals.** THEODORE W. RICHARDS (*J. Amer. Chem. Soc.*, 1911, 33, 888—893).—Analyses of cadmium sulphate by Perdue and Hulett (this vol., ii, 397) have shown that the amount of cadmium present in both the crystalline and anhydrous forms is less than that theoretically required on the basis of the atomic weight of cadmium as determined by Baxter. It is now pointed out that this discrepancy is probably due to the presence of solvent in the crystals of cadmium sulphate in the form of a solid solution, and to the retention of traces of the solvent in the dried sulphate either as solid solution or by mechanical inclusion. The presence of a solid solution of the solvent in crystals cannot be easily detected or easily eliminated, and it is therefore evident that solids obtained from an environment containing other substances, such as a solution, cannot be safely employed for exact quantitative work without further treatment.

E. G.

**Changes in Volume on Solution in Water of the Halogen Salts of the Alkalis.** GREGORY P. BAXTER (*J. Amer. Chem. Soc.*, 1911, 33, 922—940).—When a salt is dissolved in water, the volume

\* and *J. Amer. Chem. Soc.*, 1911, 33, 1027—1032.

of the solution is usually less than the sum of the volumes of the salt and the water, although in some cases it is greater. Buchanan (*Amer. J. Sci.*, 1906, [iv], 21, 25) has shown that in saturated solutions of the cesium haloids, the molecular volumes of the dissolved salts are greater than those of the solid salts, whilst the reverse is the case with the corresponding potassium and rubidium salts. Attempts to correlate the sum of the volumes of the salt and the water with the volume of the resulting solution have previously been hampered by the lack of sufficiently accurate density determinations. The data furnished by Baxter, Boylston, Mueller, Black, and Goode (this vol., ii, 557) for the haloids of lithium, sodium, and potassium, allow the magnitude of the changes of volume which occur during the solution of these salts to be calculated with considerable precision. The results obtained from these data, and also for the rubidium and cesium salts from those recorded by Buchanan (*loc. cit.*), are tabulated.

Of the fifteen salts, five, namely, the three cesium salts and lithium bromide and iodide, undergo expansion during solution, whilst the others suffer a contraction.

The causes of these changes in volume have not hitherto been adequately explained. An explanation is now advanced which is based on Richards' hypothesis of the compressibility of atoms and on hydration. It is assumed that during solution and dissociation, a salt is freed to a large extent from compression due to chemical affinity and to molecular cohesion, and that, when the ions or molecules combine with water, both the hydrated substance and the water undergo compression. The latter effect varies regularly with the compressibilities of the substances and with their mutual affinities. It is shown that the change in volume in the formation of the ions from the elements, as measured by the sum of the change in volume in the formation of the solid salt and the change in volume during solution, is an additive property. The part played by the polymerisation of water in the change of volume is discussed, and it is considered probable that this effect varies with varying temperature, but that at the temperature of the experiments quoted it is very small.

E. C.

**The Internal Frictions of Colloidal and Non-colloidal Liquids.** LUDWIG DIENES (*Biochem. Zeitsch.*, 1911, 33, 222—224).—In experiments with von Liebermann's modification of Coulomb's apparatus (this vol., ii, 585), it was noticed that the logarithmic decrement of the vibration amplitudes increases as the vibrating disc is sunk in the liquids in the case of non-colloidal substances, whereas in the case of colloids it is greatest near the surface. The author offers explanations of the phenomena.

S. B. S.

**Mode of Dissolution of Colloidal Substances.** PAUL BARY (*Compt. rend.*, 1911, 152, 1386—1387).—The author regards a colloidal solution as containing solid-liquid particles in suspension, such that the attraction between the liquid and solid is in equilibrium with the sum of the elastic tension of the particles and the surface tension. The particles may be considered as spongy cells into which

liquid has penetrated by osmosis. Coagulation in such solutions is brought about by the influence of soluble salts in effecting local alterations in osmotic pressure.

W. O. W.

**Ultra-microscopic Investigation of Certain Colloids Coagulated by Electrolytes.** GEORG WIEGNER (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 227—232).—Ultra-microscopic observations of the process of coagulation in cow's milk and in colloidal solutions of gold indicate that the nature of the process is such that the smaller colloidal particles attach themselves to larger particles, and that there is little tendency for particles of the same size to cohere. The larger ultra-microscopic particles seem to act, therefore, as coagulation nuclei for the smaller particles.

The slight differences observed in the coagulation processes in milk and in colloidal gold solutions are probably due to differences in the size of the particles which may act as coagulation nuclei in the two cases.

H. M. D.

**The Coagulum from Gelatin-Gum Arabic Sols, and its Analogy to Casein.** F. W. TIERBACKX (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 238—239. Compare this vol. ii, 378).—The swelling properties of the coagulation product obtained from solutions containing gelatin and gum arabic are described, and reference made to the similarity between these and the colloido-chemical properties of casein.

H. M. D.

**Distribution of Ammonia between Water and Chloroform.** JAMES M. BELL and ALEXANDER L. FIELD (*J. Amer. Chem. Soc.*, 1911, 33, 940—943).—The distribution of ammonia between water and chloroform has been determined at 25°, and over a much wider range of concentrations than has been studied previously. The results show that the distribution ratio varies with the concentration from about 14 in very dilute solutions to about 10 in concentrated solutions, and that it is only very slightly affected by the presence of ammonium chloride.

E. G.

**Influence of Dissolved Salts on the Distribution of a Substance between Two Solvents.** NICOLAS DE KOLOSOWSKY (*Bull. Soc. chim. Belg.*, 1911, 25, 183—210\*).—The distribution of acetic acid between water and ethyl ether has been measured for different concentrations up to the point at which the two liquids become identical. The relationship between the ratio of distribution between water and ether ( $C$ ) and the quantity of acetic acid ( $p$ ) contained in 100 c.c. of the aqueous layer is given by  $C = 2.066 - 0.0667p + 0.00106p^2$  at 18°.

In general, the presence of salts lowers the ratio of distribution, and for salts of different metals the lowering produced increases in the series: potassium, sodium, barium, magnesium. On the other hand, the acetates of the alkali and alkaline-earth metals raise the distribution ratio, and this is attributed to the formation of acid salts.

H. M. D.

\* and *Bull. Soc. chim.*, 1911, [iv], 9, 632—637.

**Solubility Equilibria between Iodine and Organic Substances.** F. OLIVARI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 470—474).—The author has investigated the complete solubility diagrams of iodine and various organic compounds in order to ascertain whether complete or incomplete miscibility, solubility in the solid state, etc., exist between the compounds, and whether any possible complex compounds are capable of crystallising or of revealing their existence by the form of the equilibrium curves.

The solubility curves of iodine in proximity to the point of fusion of this element practically coincide for iodoform, azobenzene, *p*-dibromobenzene and *p*-dinitrobenzene, and deviate somewhat for benzoic anhydride and acid, the behaviour of these two compounds being due to their molecular polymerisation (compare Abstr., 1910, ii, 18).

The curves of solubility of iodine in *p*-dibromobenzene, *p*-dinitrobenzene, benzoic anhydride and benzoic acid exhibit an extended horizontal branch corresponding with the formation of two liquid strata; fused iodine is hence not completely miscible with these organic compounds.

The solubility diagrams for *p*-dibromobenzene and azobenzene show changes of curvature at concentrations of about 70% and 60% respectively, the adjacent solutions probably passing in the neighbourhood of the critical state.

The presence of the eutectic even in dilute solutions (5–6%) excludes the possibility of isomorphism between the components beyond this limit.

Thus, the curves furnish no indication of the crystallisation of iodine complexes, and, since there are reasons (such as the red or reddish-brown colour of the liquid phase) for believing that they exist in solution, the conclusion must not be drawn that their saturation temperatures in the mixtures are below the eutectic temperatures.

T. H. P.

**Equilibrium in the System: Water, Sodium Sulphate, Sodium Chloride, Copper Sulphate, Cupric Chloride.** FRANS A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 13, 1163—1177. Compare this vol., ii, 381).—Solubility data are recorded showing the composition of the solutions saturated respectively with one, two, and three solid phases at 15°, 25°, and 35°. Within this range of temperature, the quaternary system gives rise to only one double salt,  $\text{Na}_2\text{SO}_4 \cdot \text{CuSO}_4 \cdot 2\text{H}_2\text{O}$ . By means of a spacial model, in which the solubility data are incorporated, the solid phases capable of co-existence at the different temperatures in contact with aqueous solution are clearly exhibited.

II. M. D.

**Equilibrium in the System: Water, Ethyl Alcohol, and Ethyl Ether.** SHINKICHI HORIBA (*Mem. Coll. Sci. Eng.*, 1911, 3, 63—78).—The equilibrium in the ternary system water-ethyl alcohol-ethyl ether has been determined at 25° by shaking the components together in varying proportions and finding the composition of the upper and lower layers after complete separation has taken place. The analysis of the layers was effected indirectly by means of data for the

specific gravity, index of refraction, and specific viscosity of homogeneous mixtures of the three components, which are given in tabular form. From these results and direct determinations of the binodal curve for the upper layer, the curve and tie lines representing the composition of the conjugate mixtures have been completely determined, and are represented graphically. At the critical point, the mixture contains 40% water, 28.4% alcohol, and 31.6% ether.

J. D. K.

**The So-called Nucleus and Convergence Points of the "Crystalline-liquid Phase" of *p*-Azoxyphenetole.** GEORG WULFF (*Ann. Physik*, 1911, [iv], 35, 182—184).—The peculiar structure which is exhibited by the crystalline-liquid form of *p*-azoxyphenetole when examined under the microscope can be explained on the assumption that the anisotropic phase is a colloidal solution. The nucleus points are the result of the primary coagulation, which then proceeds under the influence of the strain set up by the surface-tension, and thus leads to the production of the convergence points.

H. M. D.

**The Number of Electrons in the Atom.** HAROLD A. WILSON (*Phil. Mag.*, 1911, [vi], 21, 718—722).—Assuming the atoms to be constituted, according to Sir J. J. Thomson's theory, of spheres of positive electricity containing freely moving negative electrons, the deduction is made that the constitution of an atom containing  $n$  electrons in the positive sphere will be such that the positive sphere is divided into  $n$  equal volumes, as nearly spherical as possible, each containing a central negative electron. The electrons will thus arrange themselves on nearly spherical concentric surfaces, the distances between which are equal. Assuming that in a series of similar elements each is derived from the one preceding by the addition of one such spherical layer of electrons, and that the number of electrons is proportional to the atomic weight, the number of electrons per atom is deduced to be eight times the atomic weight of the element. The cube-root of the atomic weights plotted against the order of the element in the series fall nearly on straight lines for each series, the lines for different series being nearly parallel.

F. S.

**Classification of the Elements.** TORIBIO CÁCERES (*Anal. Fis. Quim.*, 1911, 9, 82, 121—124).—The author proposes a periodic arrangement in which the elements of the rare earths lying between lanthanum and tantalum are made part of the fifth period, which thus extends from xenon to bismuth. The suggested arrangement is not essentially different from that brought forward by Werner (compare *Abstr.*, 1905, ii, 308, 514).

G. D. L.

**Modification of the Periodic Table.** ELLIOT QUINCY ADAMS (*J. Amer. Chem. Soc.*, 1911, 33, 684—688).—The elements are arranged in six horizontal rows or periods. The first period consists of hydrogen and helium. The second contains eight elements, beginning with lithium and ending with neon. The third also contains eight elements, beginning with sodium and ending with argon. The fourth and fifth periods each contain sixteen elements, the fourth extending from



potassium to krypton, and the fifth from rubidium to xenon. The sixth period contains thirty-two elements, beginning with caesium and ending with an unknown element. Each period contains homologues of all the elements of the preceding period. Several new families of elements appear in alternate periods. The rare earths proper and the radioactive elements are not homologous to any previous elements, but are two groups of families which enter into the sixth period. Apart from the rare earth and radioactive elements, seven elements await discovery.

E. G.

**Position of the Most Important Elements in the Periodic System.** K. SCHERINGA (*Chem. Weekblad*, 1911, 8, 389—390).—The most important elements in each horizontal series of the periodic system lie on the same line, as is best illustrated by mapping out the whole system on a cylinder.

A. J. W.

**Molecular Magnitudes.** JEAN PERRIN (*Compt. rend.*, 1911, 152, 1380—1382. Compare Abstr., 1908, ii, 927; 1910, ii, 493; this vol., ii, 480).—An emulsion of resin with water and alcohol was submitted to fractional centrifugation during four months to obtain grains of uniform density. The grains had  $D\ 1.1942$  and their mean radius,  $a$ , obtained by counting the particles in a definite volume, was  $0.3667\mu$ . The radius calculated by an application of Stokes' law was  $0.368\mu$ . Their concentration at different levels in the liquid was determined by a photographic method of counting. Avogadro's constant,  $N$ , the number of molecules in a gram-molecule, was thus found to be  $68.3 \times 10^{22}$ , whence the value for  $e$ , the charge on an electron, is  $4.25 \times 10^{-10}$ .

The displacement of a grain,  $\xi$ , in the fluid of viscosity,  $\zeta$ , during time  $\tau$  was measured microscopically. Einstein's formula,  $\xi^2 = \tau(RT/N)(1/3\pi a\zeta)$ , then gave  $4.21 \times 10^{-10}$  as the value for  $e$ . This is practically identical with the number calculated from the electrification of solid spheres.

W. O. W.

**Regulator for Diminished Pressure with Periodic Alterations.** ANTOINE VILLIERS (*Chem. Zentr.*, 1911, i, 857—858; from *Bull. Sci. Pharmaceut.*, 1911, 18, 7—11).—A full description is given of an apparatus by means of which the air or gas pressure in a vessel can be varied periodically from the normal pressure down to a pressure limited only by the capabilities of the air-pump used.

T. S. P.

**Luminosity of Phosphorus: Lecture Experiments.** LUIGI MARINO and C. PORLEZZA (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 442—446).—By the following method the phosphorescence of phosphorus vapour may be rendered apparent to a large audience without the latter being inconvenienced by the fumes and without a specially darkened room. A current of carbon dioxide is passed through a saturated solution of sodium hydrogen carbonate, then dried by means of a tower containing calcium chloride, and finally passed over red phosphorus contained in a hard glass tube. The latter is first heated at its extremity, while the gas is passing slowly, until all

moisture has been eliminated. A delivery tube reaching to the bottom of a flask of about 2 litres capacity is then attached, and the gas current reduced to a minimum. When drops of white phosphorus begin to deposit on the cooler parts of the delivery tube, the flask is placed under the latter, and a strong intermittent current of carbon dioxide passed. The phosphorus vapour, coming into contact with the air of the flask diluted with carbon dioxide, generates a green flame, and the whole of the bottom of the flask appears phosphorescent.

By suitably modifying this apparatus and by employing a mixture of carbon dioxide with 10% of air, a stable, lemon-yellow substance is deposited, which is found to have the composition  $P_4O$  (compare Michaelis and Pitsch, *Abstr.*, 1899, ii, 285).

The authors draw the conclusion that, in the oxidation of phosphorus, three different stages are reached, according to the conditions employed: (1) formation of  $P_2O_5$  when phosphorus vapour burns completely in excess of oxygen; (2) formation of  $P_2O_5$  and  $P_4O$  when phosphorus is burnt in a current of air; (3) formation of a lower oxide, probably  $P_4O$ , when phosphorus is oxidised with highly diluted oxygen under the conditions of the authors' experiments.

T. H. P.

## Inorganic Chemistry.

**Constitution of Water.** JACQUES DUCLAU (Compt. rend., 1911, 152, 1387—1390).—Regarding water as a solution of ice,  $(H_2O)_n$ , in hydrol.  $H_2O$ , and supposing the ice to retain its normal density, the author attempts to find the value of  $n$  in the foregoing formula. When deduced from the variation of the coefficient of expansion of water with pressure,  $n$  is 9—12. The limits are 6—23 when derived from the variation of the coefficient of compressibility with temperature, whilst when calculated from the specific heat and expansion,  $n=12$ .

If, as Sutherland has supposed, the density of ice in solution is lower than when in the solid state, the molecular weight is possibly not higher than that corresponding with the formula  $(H_2O)_6$ .

W. O. W.

**Solubility of Water in Benzene, Petroleum, and Paraffin Oil.** ERICH GROSCHUFF (*Zeitsch. Elektrochem.*, 1911, 17, 348—354).—Benzene is dried by keeping over sodium and then by distillation over the liquid alloy of potassium and sodium. The high boiling petroleum and paraffin oil are first heated at  $120^\circ$  for some time, and finally distilled over fused sodium. The solubility is determined by sealing up the dry solvent with a known quantity of water, accurately measured by a capillary pipette, in a glass bulb, and heating until the water is dissolved; by slight supercooling a cloud is then formed, which

disappears again at a slightly higher temperature. The solubility of water in 100 grams of benzene is 0.030 gram at 3°; 0.061 at 23°; 0.114 at 40°; 0.184 at 55°; 0.255 at 66°, and 0.337 at 77°. In purified American petroleum, boiling between 190° and 250°, the solubility is much smaller, increasing from 0.0012 gram per 100 at -2° to 0.097 at 94°, whilst in the paraffin oil (distilling between 200° and 300° at 10 mm. pressure) it was 0.003 at 16° and 0.055 at 94°. The bearing of the results on the behaviour of oils when used as electrical insulators is discussed.

T. E.

**Distribution of Hydrogen Sulphide in a Large Laboratory and the Use of Aluminium Stopcocks.** EDWARD D. CAMPBELL (*J. Amer. Chem. Soc.*, 1911, 33, 947—948).—An account is given of the system of supplying hydrogen sulphide in the laboratory of the University of Michigan, which has been found to be very satisfactory. Generators of the form described by Browne and Mehling (*Abstr.*, 1906, ii, 609) are placed in the attic in a small room, which is provided with an exhaust fan operated by an independent motor. The waste pipe for carrying away the spent liquor is connected directly with the main sewer outside the building. Two generators have been installed, so that when one is being cleaned or re-charged, the other can be brought into use. The hydrogen sulphide for the generator is passed through a wash-bottle containing water and through a tower of calcium chloride, and is distributed by means of a system of ordinary gas pipes. The delivery ends of the pipes are fitted with aluminium stopcocks, which resemble ordinary laboratory gas taps, except that the hole in the tip is only about 0.5—1 mm. in diameter, so as to prevent excessive loss of the gas if the stopcock is left open. These aluminium stopcocks are not affected by dry hydrogen sulphide, and give no trouble if they are occasionally lubricated.

R. G.

**A Modification of Raschig's Theory of the Lead-Chamber Process.** EDWARD DIVENS (*J. Soc. Chem. Ind.*, 1911, 30, 594—603. Compare this vol., ii, 272).—What goes on in the lead-chambers is largely a matter of inference, but it may be inferred with certainty that, before sulphuric acid can be produced in the process, there must be combination between sulphur dioxide and nitrous acid or its equivalent. When the process is working normally, the single substance formed by the combination must decompose as fast as it is formed. The presence in the chamber of this intermediate substance will therefore be unrecognisable.

Nitrososulphuric acid (nitrosyl sulphate),  $\text{HNSO}_3$ , is not qualified to play the part of the intermediate substance, for it is no more than a compound of nitrous anhydride with sulphuric acid, the mixed hemi-anhydride of the two acids, into which it decomposes again when hydrated. It is not a sulphonc compound. Raschig's nitrosulphonic acid,  $\text{HNSO}_4$ , has probably no existence, and the evidence is all against the existence of his nitrosulphonic acid,  $\text{H}_2\text{NSO}_5$ .

The intermediate combination will be a substance necessarily equal in composition to that of the substances formulated on either side of the summary equation of the chamber-process. The double equation

will therefore be  $2\text{HNO}_2 + \text{SO}_2 = \text{H}_2\text{N}_2\text{SO}_3 = 2\text{NO} + \text{H}_2\text{SO}_3$ . Nitroxysulphuric acid,  $\text{OH}\cdot\text{N}\langle\bigcirc\rangle\text{N}\cdot\text{SO}_3\text{H}$ , are the name and constitution given to this intermediate substance, in accordance with nitroxysulphurous acid,  $\text{HN}\langle\bigcirc\rangle\text{N}\cdot\text{SO}_3\text{H}$ , given to the acid of Pelouze's potassium salt, to which it is allied, supposing it to be the same as the coloured substance studied by Sabatier and by Raschig, and seen occasionally in the acid of the Gay-Lussac tower. The acid  $\text{H}_2\text{N}_2\text{O}_3$ , salts of which were discovered by Thum and by Angeli, appears to be the substance of which nitroxysulphuric acid is the sulphonic derivative. Instead of calling it azohydroxyl (Thum) or nitrohydroxamic acid (Angeli), the author suggests nitroxous acid and  $\text{HN}\langle\bigcirc\rangle\text{N}\cdot\text{OH}$  as being the suitable name and constitution for it.

It is no longer necessary to assume that nitric oxide unites with only enough oxygen to form nitrous anhydride,  $\text{N}_2\text{O}_3$ , although much more is present in the chambers. For, by applying the experimental knowledge gained by Raschig, it becomes evident that the nitric oxide does combine with enough oxygen to form a substance of the composition  $\text{N}_2\text{O}_4$ , which, although it soon becomes ordinary nitric peroxide, behaves for a time as the peroxide of nitrous acid,  $\text{ONO}\cdot\text{ONO}$ , yielding, in its interactions, nitrous acid and free oxygen. Thus, the nitric oxide oxidises, as it should, to  $(\text{iso})\text{N}_2\text{O}_4$ , but the product behaves as nitrous acid.

The mist in the chambers consists, with continual resolution into drops and continual renewal, of minute particles of liquid sulphuric acid, each surrounded with its atmosphere of undiluted nitric oxide, the particle and its atmosphere being joint products of the decomposition of nitroxysulphuric acid. The nitric oxide then becomes nitrous peroxide, nitrous acid, and, completing the cycle, nitroxysulphuric acid again.

An important feature of the above theory is that only one intermediate substance, nitroxysulphuric acid, is assumed. T. S. P.

**New Methods of Preparing Colloidal Selenium Solutions.**  
ALFREDO POCHETTINO (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 428—433).—Colloidal selenium solutions have been prepared previously by reduction methods or electrical means. The method now described by the author admits of the preparation of colloidal suspensions of selenium in the most varied indifferent solvents, either solid or liquid, those employed being retene, fluorene, phenanthrene, anthracene, naphthalene,  $\alpha$ -naphthol,  $\alpha$ -naphthylamine, diphenylmethane, diphenylamine, triphenylamine, phenol, thymol, and paraffin. The solvent is heated to about its boiling point (above the melting point of selenium) in presence of selenium, the liquid assuming an increasingly dark red coloration. When solidified, the solution appears red by reflected, and blue by transmitted, light, this double coloration being characteristic of colloidal suspensions of selenium with large particles. These solutions can be repeatedly solidified and liquefied without alteration of their properties. Even when the solid suspension in anthracene or

phthalic acid is melted, the selenium does not pass into the grey crystalline condition, although the points of fusion of these solvents are higher than the transformation temperature. The higher the temperature reached in the preparation of these solutions and the slower the cooling, the smaller are the selenium granules.

When these solutions are dissolved in other solvents, the selenium passes into the new solvent liquid in a condition of marked dispersion. All the suspensions thus prepared show the double coloration, and the magnitude of the particles depends on the natures of the two solvents.

If platinum electrodes, placed in such a colloidal suspension, are connected to the poles of a Wimshurst machine, the selenium is deposited in a highly adherent, compact layer on the electrode joined to the positive pole. In some cases, however, the solvent employed may influence this phenomenon. Thus, with solutions made in the first place with phenanthrene, that in benzene always gives a deposit at the positive and that in carbon disulphide at the negative pole.

When heated the particles of disperse selenium become decomposed, the resultant particles diminishing in size as the temperature rises.

Characteristic for these solutions is the behaviour of their electrical resistance, which remains constant for a 1% solution, but gradually increases for a 0.3% or more dilute solution.

T. H. P.

**Tellurium. I. Action of Sulphuryl and Thionyl Chlorides on Tellurium.** BÉLA VON HORVÁTH (*Zeitsch. anorg. Chem.*, 1911, 70, 408—413).—Tellurium, prepared by the repeated reduction of purified telluric acid in hydrogen, reacts with sulphuryl chloride at the ordinary temperature. In an atmosphere of carbon dioxide at a red heat, tellurium tetrachloride and sulphur dioxide are formed. The same products, together with sulphur, are obtained from thionyl chloride and tellurium.

C. H. D.

**Production of Ammonia and the Economy of Nitrogen with Peat.** HERMAN CHARLES WOLTERECK (*Compt. rend.*, 1911, 152, 1245—1247. Compare Abstr., 1908, ii, 174, 400).—It has been suggested that the author's synthesis of ammonia from water and atmospheric nitrogen by passing these through peat depends solely on the action of water on the peat. It is now stated, however, that in the absence of free nitrogen less than one-third the amount of ammonia is formed than under similar conditions when it is present.

W. O. W.

**Electrolysis of Aqueous Ammonia.** FRIEDRICH C. G. MÜLLER (*Chem. Zentr.*, 1911, i, 626; from *Zeitsch. physik.-chem. Unterr.*, 1911, 23, 355—356).—Several irregularities occurring in the electrolysis of aqueous solutions of ammonia are noted. At an iron anode, oxygen, and not nitrogen, is evolved. Small quantities of ammonium nitrate may be produced during the electrolysis, which then play a considerable part in the conduction of the current.

T. S. P.

**The Preparation and Estimation of Nitric Oxide and its Behaviour towards Water.** L. MOSER (*Zeitsch. anal. Chem.*, 1911, 50, 401—433).—An investigation of the various methods for the

preparation of nitric oxide leads the author to the conclusion that the pure gas is best obtained either by the reduction with mercury of nitrous acid dissolved in sulphuric acid, or by the interaction of hydriodic acid and nitrous acid. The nitric oxide so obtained cannot be preserved unchanged over water; chemical reactions take place which are due, in part, to the oxygen dissolved in the water, and in part to the hydrions contained in the water. Nitrous and hyponitrous acids are formed, probably according to the equation:  $4\text{NO} + 2\text{H}_2\text{O} \rightleftharpoons 2\text{HNO}_2 + \text{H}_2\text{N}_2\text{O}_2$  (compare Zimmermann, Abstr., 1906, ii, 82), which then decompose, the latter acid giving, not only nitrous oxide, but also ammonium nitrite ( $3\text{H}_2\text{N}_2\text{O}_2 = 2\text{N}_2\text{O}_3 + 2\text{NH}_3$ ; compare Hantzsch and Kaufmann, Abstr., 1897, ii, 25), which breaks down with the liberation of nitrogen. The quantity of nitrogen increases the longer the nitric oxide is preserved over water. Nitric oxide, whether moist or dry, can be preserved over mercury at room temperature for any length of time without undergoing a change.

Pure nitric oxide is completely absorbed by a solution of ferrous sulphate, but the results are inaccurate in the presence of nitrous oxide. Ferrous sulphate cannot be advantageously replaced by a slightly alkaline solution of sodium sulphide (compare Divers, Trans., 1899, 75, 82), since the reaction is much slower, and the absorption is complete only after long shaking.

The volumetric determination of nitric oxide by means of permanganate, as carried out according to Lunge (*Zeitsch. angew. Chem.*, 1890, 567), generally gives too low results; small quantities of nitric oxide cannot be determined at all. The author modifies the method in such a way that the gas to be analysed is passed into an absorption vessel previously full of standard permanganate solution; after shaking well to complete the reaction, the diminution in the strength of the permanganate is measured. All errors caused by using a current of indifferent gas to sweep the nitric oxide through the permanganate solution are thus avoided. The same apparatus may be used with hydrogen peroxide in place of permanganate, the nitric acid formed by the oxidation of the nitric oxide being determined by titration with standard alkali. The method gives good results as long as the presence of acid vapours or gases is avoided.

The method of combustion after mixing with hydrogen gives inconstant results, owing partly to the formation of ammonia as a by-product, and partly to the permeability towards gases of platinum heated to a red heat.

T. S. P.

Formation of Nitrosyl Chloride at Low Temperatures by Gay Lussac's Reaction. Liquidus Curve of the System Nitrosyl Chloride-Chlorine. N. BOURNOFF and PHILIPPE A. GUYE (*J. Chim. Phys.*, 1911, 9, 290-313).—The formation of nitrosyl chloride at low temperatures by direct interaction of chlorine and excess of nitric oxide was studied quantitatively with a view to estimating the atomic weight of chlorine by this method. The excess of nitric oxide having been removed by distillation at the temperature of liquid pentane ( $-160^\circ$  to  $-150^\circ$ ), the nitrosyl chloride was found to contain 3 to 4% of chlorine more than the formula

$\text{NOCl}$  indicates. When excess of chlorine is used for the synthesis, the same product is obtained. The excess of chlorine is readily removed by fractional distillation at higher temperatures than  $-80^\circ$ , but is retained at  $-150^\circ$ .

The existence of higher nitrosyl chlorides, such as  $\text{NOCl}_2$ , having been discredited by Tilden and others, it must be supposed that a highly dissociated additive compound of nitrosyl chloride and chlorine is formed. The liquidus curve of the mixed gases was determined, the liquids being distilled from weighed glass bombs into a special cryoscopic tube. The mixtures were agitated by a glass stirrer operated magnetically by an iron core fused into the upper part. All joints in the apparatus were made with ground glass flanges well greased and held together with screw clips. The mercury in the manometers was protected by a layer of syrupy phosphoric acid. The liquidus curve exhibits no maxima, but there is also no sharp minimum at the eutectic point, about  $-109^\circ$ . The curve is well rounded here, indicating the presence of a compound of approximate composition  $\text{NOCl}_2$ , which is highly dissociated even at  $-107^\circ$ .

It is suggested that the presence of excess of chlorine in the authors' synthetic nitrosyl chloride is due to the incompleteness of the reaction at the low temperatures employed.

R. J. C.

**Preparation of Certain Nitrides by Reduction of Alkaline Cyanides.** ALEXANDER C. VOURNASOS (*Bull. Soc. chim.*, 1911, [iv], 9, 506—512).—A résumé of methods for the preparation of metallic nitrides is first given, and it is then pointed out that certain elements, such as boron and aluminium, decompose cyanogen or hydrocyanic acid at  $750^\circ$ , forming nitrides. The corresponding nitride is produced when boron, aluminium, cerium, or lanthanum in a finely divided state is added to fused potassium cyanide.

The potassium cyanide is first melted in a porcelain crucible at  $650^\circ$  in the absence of air, and poured out on a marble slab. It is then re-melted in a clay or porcelain crucible, and the dry, finely-powdered element added in portions, the mixture being agitated from time to time, and the heating continued for fifteen minutes after the final addition. The cooled black mass is placed in warm water, and the insoluble residue of nitride and amorphous carbon is carefully and gently ignited in air to remove the carbon.

Boron nitride,  $\text{BN}$ , so prepared, is a white powder, which is attacked with difficulty by warm water. Cold water slowly becomes alkaline in contact with the nitride, due to the formation of ammonia. Aluminium nitride,  $\text{Al}_2\text{N}_3$ , is an amorphous, yellow powder. Cerium nitride,  $\text{CeN}$ , is readily oxidised, and consequently the carbon produced along with it cannot be removed by ignition in air. Lanthanum nitride resembles the cerium compound. Both are readily decomposed by warm water, yielding ammonia.

T. A. H.

**Amorphous States of Silicon.** LIVIO CAMBI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 440—442).—The amorphous silicon obtained by the author from the black sulphide (see following abstract) is distinguished from those previously described in possessing a paler

reddish-yellow colour, different from the greyish-yellow tint sometimes assumed by crystalline silicon. The product containing 96% Si has D 2.08 (compare Vigouroux, *Abstr.*, 1895, ii, 222, 263; Wilke-Dörfurt, *Abstr.*, 1910, ii, 204). When heated, the properties, such as colour and specific gravity, of the author's product approach those of Vigouroux's silicon.

These amorphous silicones must be regarded, not as clearly defined allotropic forms, but as masses of forms possibly possessing different molecular structures.

T. H. P.

**Silicon Sulphides.** II. LIVIO CAMBI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 433—440).—The author has studied the hydrolysis of the black and yellow silicon sulphides previously obtained (*Abstr.*, 1910, ii, 952).

The yellow sulphide yields silicoformic anhydride,  $(\text{SiHO})_2\text{O}$ , the corresponding acid being probably formed first:  $\text{SiS} + 3\text{H}_2\text{O} = \text{SiHO}\cdot\text{OH} + \text{H}_2\text{S}$ . The silicon in the sulphide hence acts as a bivalent element. The formation of silicoformic acid is analogous to that of formic acid, which can be obtained from chloroform, carbon monoxide, or compounds containing bivalent carbon, such as the carbylamine derivatives,  $\text{C}\cdot\text{NR}$ ; this analogy can be extended to the corresponding germanium compounds. The action of dry hydrogen chloride on the yellow sulphide yields hydrogen sulphide and silicochloroform. The properties of this sulphide fall into line with those of the sulphides of the other elements of the second half of the fourth group; for example, the orange-yellow colour of the silicon compound becomes reddish-brown for germanium, dark brown for tin, and black for lead.

The vitreous, black silicon sulphide (*loc. cit.*) undergoes dissociation:  $2\text{SiS} \rightarrow \text{Si} + \text{SiS}_2$ , which may be more or less complete, the presence of unaltered monosulphide and possibly, also, of intermediate labile compounds similar to  $\text{P}_2\text{S}_5$ , not being excluded. On hydrolysis it yields soluble silica and amorphous silicon (see preceding abstract).

T. H. P.

**The Electrical Conductivity and Behaviour of Diamond at High Temperatures.** CORNELIO DOELTER (*Monatsh.*, 1911, 82, 275—298).—The electrical conductivity of diamond has been measured at temperatures between 880° and 1290° in an atmosphere of nitrogen or hydrogen. For a plate 1 square cm. in area and 1 mm. thick, the resistance falls from 58800 ohms at 950° to 370 ohms at 1220°, then increases to 930 ohms at 1260°, and again falls to 590 ohms at 1290°. This behaviour is somewhat similar to that exhibited by quartz.

The reputed conversion of diamond into graphite at high temperatures is discussed, and the microscopic appearance of the diamonds used in some earlier experiments is described. These observations afford no evidence of the formation of graphite. New experiments, in which diamonds were heated in carbon dioxide at 1350°, in hydrogen at 1300° to 1550°, in nitrogen at 1300°, and in chlorine at 1200°, have also failed to give evidence of conversion into graphite. At these temperatures the diamonds acquire a brownish-black colour in certain cases, but this appears to be due to amorphous carbon. The effect is



probably one of corrosion, and if sufficiently protected it seems likely that the diamond remains unchanged at temperatures of 2000—2500°.

H. M. D.

**Action of Carbonyl Chloride on Natural and Artificial Sulphides.** ÉDOUARD CHAUVENET (*Compt. rend.*, 1911, 152, 1250—1252. Compare Abstr., 1909, ii, 53; this vol. ii, 109).—Carbonyl chloride attacks metallic sulphides between 300° and 450° in accordance with the equation  $MS + COCl_2 = MCl_2 + COS$ . The ease with which sulphides are thus converted into anhydrous chlorides furnishes a useful method for the treatment of minerals in analysis. The process is also suitable for preparing carbonyl sulphide.

W. O. W.

**Ratio of Argon to Nitrogen in Natural Gaseous Mixtures and its Significance.** CHARLES MOUREU and ADOLPHE LEPAPE (*Compt. rend.*, 1911, 152, 1533—1535. Compare this vol. ii, 392, 439).—The ratio of argon to nitrogen in natural gaseous mixtures from fifty-two mineral springs was determined and found to be fairly constant. In thirty-six springs  $100A/N = 1.0 - 1.29$ ; the same ratio for air is 1.18. Geologically nitrogen behaves as an inert gas, and adopting the view expressed in a previous communication it would appear that the greater part of the gas has existed in the free state from the origin of the earth.

W. O. W.

**Luminescent Tubes of Neon.** GEORGES CLAUDE (*Compt. rend.*, 1911, 152, 1377—1379).—The luminescence of tubes containing neon traversed by an alternating current gradually diminishes, owing to absorption of gas. It has been found that copper electrodes of small size become red hot, the metal rapidly volatilising and becoming deposited on the sides of the tube. The deposit produced in this way yields a gas when dissolved in nitric acid; in one experiment, 1.6 grams gave 2.5 c.c. of gas, whilst the same weight of unvolatilised electrode gave only 0.3 c.c. The latter contained a little neon, but no helium, whilst the gas from the deposit showed an intense spectrum of neon and helium. The two gases appeared to be present in about equal amounts, although the neon with which the tube was filled contained originally only a trace of helium.

The suggestion is offered that helium results from the dissociation of neon, or else that the greater part of the neon absorbed by copper is not liberated when the metal is dissolved in nitric acid.

By increasing the surface of the electrodes, absorption of gas is considerably diminished. Thus a tube 35 metres long and 45 mm. diam., with electrodes of area 3 sq. cm. per ampere, remained luminous for 210 hours, when an accident terminated the experiment.

W. O. W.

**Preparation of Alkali Metals.** LOUIS HACKSPILL (*Bull. Soc. chim.*, 1911, [iv], 9, 446—451).—Detailed descriptions of the apparatus and method of working are given for the reduction of alkali chlorides by means of metallic calcium as already described (Abstr., 1905,

ii, 585). The prepared mixture of calcium and the alkali chloride is placed in an iron tube lying in a glass tube, which can be rendered vacuum. The glass tube is heated to the required temperature in a simple electric furnace of special form. Potassium, cesium, and rubidium have been prepared in this way. Attempts to prepare lithium were unsuccessful, but by using a modified form of Guntz's apparatus, an alloy of lithium with 3 or 4% of calcium was obtained.

T. A. H.

**Solubility of Sodium Carbonate.** C. H. KETNER (*Chem. Weekblad*, 1911, 8, 391—393. Compare Abstr., 1902, ii, 308.)—The author calls attention to his work on equilibrium in the system sodium carbonate, alcohol, water—which seems to have been overlooked.

A. J. W.

**Hydrates of Rubidium and Cæsium Fluorides.** ROBERT DE FORCRAND (*Compt. rend.*, 1911, 152, 1208—1211. Compare this vol., ii, 488).—A saturated solution of rubidium fluoride deposits crystals of a hydrate,  $2\text{RbF} \cdot 3\text{H}_2\text{O}$ , m. p.  $36^\circ$ ; the heat of dissolution at  $15^\circ$  is  $-0.62$  Cal. When dried over phosphoric oxide, it forms the hygroscopic compound,  $3\text{RbF} \cdot \text{H}_2\text{O}$ , having a heat of dissolution  $3.76$  Cal. at  $15^\circ$ .

Cæsium fluoride forms two hydrates,  $2\text{CsF} \cdot 3\text{H}_2\text{O}$ , heat of dissolution  $0.99$  Cal., and  $3\text{CsF} \cdot 2\text{H}_2\text{O}$ , heat of dissolution  $4.23$  Cal.; there is no compound intermediate between the two.

The general conclusion drawn from these observations and those previously published is that in respect to the hydration of its salts rubidium does not stand invariably intermediate between potassium and cesium, but resembles sometimes one and sometimes the other in its properties.

When estimating rubidium and cesium by conversion into their sulphates, it is necessary that the temperature of ignition should not exceed  $1000^\circ$ , otherwise volatilisation occurs. Cæsium sulphate is appreciably volatile at the temperature of the blowpipe. W. O. W.

**Specific Gravity of Ammonium Sulphate Solutions.** M. C. DEKHUYZEN (*Zeitsch. physiol. Chem.*, 1911, 72, 167—168).—The expression  $^{\circ}P_{s,n}$  is used to denote the number of grams of a substance dissolved in 100 grams of solvent, and  $^{\circ}P_{s,s}$  the number of grams of solute in 100 grams of solution. If  $p$  = the first quantity and  $p_1$  the second, then  $100p/100 + p = p_1$ . The expression  $^{\circ}V_{s,s}$  expresses the number of grams of solute in 100 c.c. of solution, and if represented by  $p_2$  and density of solution by  $D$ , then  $p_2 = p_1 D$ . Wiener (this vol., ii, 394) has confused the expression  $^{\circ}P_{s,s}$  and  $^{\circ}V_{s,s}$ . J. J. S.

**Preparation of Ammonium Selenate: a New Method.** FRANK C. MATHERS and ROY S. BONSLIE (*J. Amer. Chem. Soc.*, 1910, 33, 703—708).—The only method described hitherto for the preparation of ammonium selenate is by the action of ammonia on selenic acid, but this is unsatisfactory on account of the difficulty of preparing pure selenic acid. It has now been found that the salt can be readily prepared by treating barium or lead selenate with

ammonium carbonate, and the best conditions have been determined in each case.

The barium or lead selenate is placed in a beaker with water and powdered ammonium carbonate. If barium selenate is used, for each gram of the salt 2.8 grams of ammonium carbonate (equivalent to 5 mols.) and 10 c.c. of water are employed. The mixture is left for thirty hours with occasional shaking, a yield of about 96–97% being thus obtained. In the case of lead selenate (1 gram), 0.55 gram of ammonium carbonate (equivalent to 1.2 mols.) and 5 c.c. of water are added, and the mixture left for one to two hours, when a yield of about 95–96% is obtained. Good yields can be obtained, however, in fifteen to thirty minutes. Lead selenate is therefore preferable to the barium salt for the purpose. The yield is not increased by heating the mixture or by agitating it by means of a current of air or carbon dioxide.

E. G.

**Fusion Experiments with Some Metasilicates.** PETTA LEBENDEFF (*Zeitsch. anorg. Chem.*, 1911, 70, 301–324).—Mixtures of calcium metasilicate and calcium sulphide solidify to form solid solutions. It has not been found possible to investigate mixtures containing more than 50% of calcium sulphide on account of their corrosive action. Calcium sulphide is infusible in a kryptol furnace. The solid solutions undergo a transformation at temperatures below their freezing point, the transformation curve having a maximum at about 1300° and 20 mol. % of calcium sulphide. Rapidly cooled mixtures disintegrate completely when cold, whilst slowly cooled mixtures show, when examined microscopically, separate crystals of the pseudo-hexagonal modification of wollastonite and of calcium sulphide, identical with the oldhamite found in meteorites.

Magnesium and manganese metasilicates form two series of solid solutions, with a break in the freezing-point curve at 1328° and 50 mol. %  $\text{MgSiO}_3$ . The melting point of magnesium metasilicate is 1535°, and of manganese metasilicate 1210°. The optical examination shows that the crystals at the magnesium end of the series have the properties of enstatite, and those at the manganese end the properties of rhodonite, confirming the representation of the system as one of two series of solid solutions.

Calcium metasilicate, m. p. 1512°, and barium metasilicate, m. p. 1438°, form an isomorphous series, with a continuous freezing-point curve, having a minimum at about 35 mol. %  $\text{BaSiO}_3$  and 1000°. A glass is obtained on cooling rapidly, whilst slowly cooled mixtures solidify to a homogeneous series of monoclinic solid solutions, which do not disintegrate or undergo further change. Barium and manganese metasilicates are isomorphous, and the freezing-point curve has a minimum, but its exact determination is impracticable, owing to the readiness with which a glass is formed.

Experiments with mixtures of manganese metasilicates with strontium and sodium metasilicates, as well as with those already mentioned, show that glass is formed when several silicates are melted together, even when the components crystallise well, and that the tendency to the formation of glass is greatest in eutectic mixtures and in solid solutions near to a minimum point. Mixtures having

such compositions are highly viscous in the neighbourhood of the melting point. This confirms Vogt's views on the formation of glasses.  
C. H. D.

**The Causes of the Variation in the Velocity of Hydration of Cement.** PAUL ROHLAND (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 251—253).—Measurements of the rate of hydration of cement in contact with aqueous solutions show that sodium carbonate, aluminium chloride, and potassium sulphide accelerate the hydration process, whereas potassium dichromate, sodium borate and sulphates (with the exception of aluminium sulphate and the alums) retard it. The setting of the cement is not, however, solely determined by the velocity of hydration, but is influenced by the rate at which coagulation of the hydrolytically separated hydroxides of aluminium, iron, and silicon takes place. This process is also affected by the nature of the electrolytes present and by the temperature.  
H. M. D.

**Barium Sulphate a Plastic Substance.** ALBERT ATTERBERG (*Zeitsch. angew. Chem.*, 1911, 24, 928—929).—The author defines a substance as plastic when its mixture with water can be rolled out into wire, the quantity of water not exceeding that which it is necessary to add to the substance in order to make it flow.

The "flow-limit" for ordinary precipitated barium sulphate is 22 parts of water to 100 parts of sulphate, whilst the "rolling-out limit" is 14 parts of water to 100 of sulphate. Barium sulphate is thus a plastic substance (plasticity = 8).

Further experiments have shown that minerals, such as kaolinite, potassium and magnesium micas, talc, etc., are strongly plastic when they are ground so finely that the size of their particles does not exceed 0.002 mm.; under the same conditions, minerals, such as quartz, felspar, and calc spar, show no plasticity. It is, therefore, the presence of fine particles of minerals which occur in laminated or shaly forms which confer plasticity on clay.  
T. S. P.

**Crystallographic Examination of Fluorides Obtained by Moissan and Pupils.** AUGUST DE SCHULTEN (*Compt. rend.*, 1911, 152, 1261—1263. Compare this vol., ii, 486).—The results of crystallographic measurements are given for the fluorides of barium, strontium, manganese, nickel, cobalt, iron, and chromium; also for the double fluorides of nickel, cobalt, zinc, and calcium of the type  $MF_2 \cdot 2KF_2$ , and for the compound  $Cr_2F_6 \cdot 6KF_2$ .  
W. O. W.

**Presence of Zinc Nitride in Zinc Powder and Commercial Zincs.** CAMILLE MATIGNON (*Compt. rend.*, 1911, 152, 1309—1312).—A number of specimens of zinc dust were distilled with aqueous potassium hydroxide and the liberated ammonia determined. The amount of nitrogen found corresponded with about 0.4% of zinc nitride,  $Zn_3N_2$ . The latter was present to the extent of 1.2% in a dust prepared in such a way as to favour the formation of nitride. Commercial fused zincs were found to contain only traces of nitride, whilst this was absent from zinc oxide prepared by burning the metal in air.  
W. O. W.

**Thermal Analysis of Mixtures of Cuprous Chloride with Chlorides of Univalent Elements.** C. SANDONNINI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 457—464).—The author has studied the melting-point diagrams of mixtures of cuprous chloride with silver, sodium, potassium, or thallous chloride, the solidification temperatures for these salts being found from the cooling curves to be  $422^{\circ}$ ,  $455^{\circ}$ ,  $806^{\circ}$ ,  $776^{\circ}$ , and  $429^{\circ}$  respectively.

The results show that cuprous chloride forms solid solutions, in limited degree, with the chlorides of the metals of the second half of the first group, homologous with copper, sodium, and silver. Double salts of the type  $\text{CuCl}_2\cdot\text{MCl}$  are formed with potassium and thallous chlorides, whilst mixed crystals are formed, within very restricted limits, between cuprous and thallous chlorides.

T. H. P.

**Binary Systems of the Chlorides of Certain Univalent Metals.** G. POMA and G. GABBI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 464—470).—The authors have studied the cooling curves of the systems  $\text{CuCl-KCl}$  and  $\text{CuCl-AgCl}$  (compare Sandonnini, preceding abstract), the fusions being effected in an atmosphere of nitrogen, owing to the extreme oxidisability of cuprous chloride. The values found for the m. p.'s are:  $\text{CuCl}$ ,  $415^{\circ}$ ;  $\text{AgCl}$ ,  $451^{\circ}$ ; and  $\text{KCl}$ ,  $759^{\circ}$ .

In the liquid state, cuprous and silver chlorides are completely miscible, but in the solid state there is a very wide gap in the solubility. From the fused mixtures, no compound of the two components separates on cooling.

In the case of cuprous and potassium chlorides, the fusion curve exhibits two arrests ( $142^{\circ}$  and  $236^{\circ}$ ), and has the form characteristic for binary systems, in which the two components form a compound which dissociates at a high temperature. The compound formed has probably the formula  $\text{K}_2[\text{CuCl}_2]$ .

T. H. P.

**The Binary Systems,  $\text{CuCl-AgCl}$ ,  $\text{CuCl-NaCl}$ ,  $\text{CuCl-KCl}$ .** PIETRO DE CESARIS (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 597—599).—The author's investigation of the melting-point curve of the system  $\text{CuCl-AgCl}$  gives results in good agreement with those obtained by Sandonnini and by Poma and Gabbi (preceding abstracts).

The results for  $\text{CuCl-NaCl}$  give a curve very similar to that obtained by Sandonnini (*loc. cit.*), but differing from it in certain details.

For the system  $\text{CuCl-KCl}$  the author's results confirm Sandonnini's conclusion that these salts form the compound  $\text{CuCl}_2\cdot 2\text{KCl}$ .

T. H. P.

**Catalytic Action of Copper Oxide.** JAMES STRACHAN (*Chem. News*, 1911, 103, 241. Compare Sabatier, *Abstr.*, 1909, i, 546).—Over a year ago the author noticed a similar action in the case of a Barthel spirit bunsen to that recently observed by Meunier (this vol., ii, 205) with an ordinary bunsen. The efficiency of such a burner becomes impaired in time by surface-combustion on the partly oxidised brass gauze, necessitating replacement of the latter. On extinguishing the burner, the gauze continues to glow so long as methylated spirit-vapour and air impinge on it. That surface-

combustion commences at a low temperature may be shown by interrupting the stream of spirit-vapour for a few seconds. The combustion re-commences on the most oxidised portions of the gauze, proceeding rapidly over its whole surface. A strong odour of aldehyde is produced.

Various lecture experiments with asbestos fibre, alternately dipped in copper sulphate solution and ignited, are described. Asbestos so treated will ignite an explosive mixture of hydrogen and oxygen if fairly hot.

Other metallic oxides show like properties, and the experiments may be repeated, replacing copper sulphate by ferric chloride, but the ferric oxide so produced does not seem quite so active as copper oxide. It is pointed out that this catalytic action of ferric oxide may prove a source of danger with miners' safety lamps, in most of which iron gauze is used.

The author states that the mutual catalytic action of cellulose and copper oxide is one factor in the formation of dendritic growths of the latter on paper.

J. D. K.

**Elements in Thulium.** CARL AUER VON WELSBACH (*Monatsh.*, 1911, 32, 373—375).—Spectroscopic examination indicates that thulium consists essentially of three elements. Of these three, thulium I. and thulium III. cannot be isolated by the present methods of purification. The salts of the former absorb rays in the extreme red down to  $\lambda$  700, and show characteristic lines (quoted) between 2700 and 3270 (spark spectrum). Thulium III. exhibits a characteristic spark spectrum between 2800 and 3260.

The author hopes to isolate pure thulium II. in the near future. It forms an almost white sesquioxide. Its salts are pale yellowish-green in daylight and emerald-green in artificial light, and exhibit the absorption spectrum hitherto ascribed to thulium. The oxides of those fractions which are richest in thulium II. and aldebaranium exhibit a characteristic phenomenon in the flame; before becoming actually incandescent the oxides give out a purple light for a short time. The spark spectrum shows many strong lines (quoted) between 3400 and 3800.

C. S.

**The Chemical Constitution of the Kaolinite Molecule.** JOSEPH W. MELLOR and A. D. HOLDCROFT (*Trans. Eng. Ceramic Soc.*, 1911, 10, 94—120).—Contrary to what is generally accepted, there is no definite temperature above which it can be said that kaolinite decomposes, and below which kaolinite does not decompose. The effect of raising the temperature is to accelerate the speed of decomposition, a result which can also be obtained by working under diminished pressure. The speed of decomposition at 500° is sufficiently rapid at atmospheric pressure to decompose an appreciable quantity of kaolinite in an hour.

The heating curve of kaolinite shows that an endothermic reaction occurs in the vicinity of 500°, and an exothermic reaction just above 800°; the curve shows no sign of the dehydration taking place in stages, such as might occur if the elements of the "combined

water<sup>4</sup> were placed unsymmetrically in the molecule. In the absence of other evidence, and since solubility determinations show no sign of unsymmetrical aluminium groups, it is assumed that the hydroxyl and aluminium groups are symmetrically placed in the molecule, and the formula  $\begin{matrix} (HO)_2 \\ (HO)_2 \end{matrix} \gg Al_2 \begin{matrix} O-SiO \\ O-SiO \end{matrix} O$  is suggested for kaolinite.

The solubility in acids, the hygroscopicity, and the density of kaolinite calcined at different temperatures, show that there is a certain parallelism in the properties of alumina and calcined kaolinite. The exothermal change indicated by the heating curve of kaolinite corresponds with that furnished by alumina derived from aluminium nitrate. The endothermal change shown in the heating curve in the neighbourhood of 500° corresponds with a decomposition of kaolinite into free silica, free alumina, and water. The restoration of from 3—4% of water to calcined kaolinite, which can be accomplished by heating it under pressure in steam, corresponds with a re-hydration of silica or alumina.

When kaolinite is heated to over 1200°, sillimanite is formed by the re-combination of the free alumina with some of the free silica formed at about 500°. The exothermal change in the heating curve at 800° corresponds with a physical change of the free alumina, which becomes less soluble in acid, less hygroscopic, and more dense.

Kaolinite may be represented as one member of a series of aluminodisilicic acids, and these in turn form one group of a large number of alumino-silicates, comprising alumino-mono-, di-, tri-, tetra-, penta-, and hexa-silicates, the different classes of which may be represented, for example, by allophane, kaolinite, natrolite, pyrophyllite, chabazite, and orthoclase respectively. T. S. P.

**The System Manganous Oxide-Silica.** FRIEDRICH DOERINGEL (*Metallurgie*, 1911, 8, 201—209).—Mixtures containing from 20 to 60 mol. % of silica may be prepared in a platinum crucible, embedded in magnesia. Mixtures containing more manganese attack the platinum, whilst those richer in silica require too high a temperature. It is necessary to melt the mixture a second time to obtain complete reaction. Three crystalline constituents are observed in the sections obtained, namely: manganosite, MnO; tephroite, Mn<sub>2</sub>SiO<sub>4</sub>; and rhodonite, MnSiO<sub>3</sub>, identical with the naturally-occurring minerals. The thermal results indicate that tephroite is formed by a reaction at 1323° between some primary crystals and the liquid, and that, also, in mixtures containing 49—60 mol. % of silica, primary crystals rich in silica react with the liquid at 1215° to form rhodonite. The tephroite-rhodonite eutectic point is at 1190° and 45 mol. % SiO<sub>2</sub>. C. H. D.

**Existence of a New Type of Dioxides: Reaction between Selenious Acid and Manganese Dioxide.** LUIGI MARINO and V. SQUINTANI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 447—452. Compare Marino, Abstr., 1908, ii, 106).—The authors find that the compound obtained by Laugier (Abstr., 1887, 775) by the action of

selenious acid on manganese dioxide in a sealed tube at  $140^{\circ}$  is the selenite corresponding with the dioxide,  $\text{MnSe}_2\text{O}_6$ , the other products observed by Laugier being formed by the decomposition of this compound. This selenite, which is obtained as an orange-yellow, crystalline powder, liberates chlorine from dilute or concentrated hydrochloric acid, and iodine from potassium iodide solution containing acetic acid. With alkali hydroxides or carbonates, manganese dioxide is set free, whilst with oxalic acid solutions, carbon dioxide is liberated quantitatively. It oxidises mercurous to mercuric salts, cuprous salts to the cupric state, potassium ferrocyanide to ferricyanide, and arsenious to arsenic acid. In presence of a slight excess of alkali hydroxide, it decomposes quantitatively according to the equation:  $\text{MnSe}_2\text{O}_6 = \text{MnO}_2 + 2\text{SeO}_2$ . Attempts to prepare a selenium acid corresponding with dithionic acid were unsuccessful.

When heated, the selenite decomposes in the following manner:  $\text{MnSe}_2\text{O}_6 = \text{SeO}_2 + \text{MnSeO}_4$ . At a higher temperature and in a vacuum, however, the decomposition proceeds according to the equation:  $5\text{MnSe}_2\text{O}_6 = 8\text{SeO}_2 + 2\text{MnSeO}_4 + \text{Mn}_3\text{O}_4 + \text{O}_2$  T. H. P.

**The Gas Contained in Steels.** GEORGES CHARPY and S. BONNEROT (*Compt. rend.*, 1911, 152, 1247—1250).—The amount of gas obtained by heating different varieties of steel at  $950^{\circ}$  in a vacuum has been determined, taking special precautions to prevent the access of water vapour. The disengagement of gas was continuous during five days, but tended towards a limit. Hard and soft steels showed the same critical points after treatment as before the removal of gas.

W. O. W.

**Cementation of Nickel Steel.** I. FEDERICO GIOLITTI and F. CARNEVALI (*Atti R. Accad. Sci. Torino*, 1911, 46, 409—432).—The authors have applied the methods previously employed in the investigation of carbon steels (*Abstr.*, 1909, ii, 240; 1910, ii, 507, 616, 780) to the study of steels containing from 2.03% to 29.8% of nickel, the gases employed for cementation being pure ethylene and carbon monoxide.

The results show that the maximum content of carbon in the cementation zone diminishes continuously as the proportion of nickel present increases, the diminution becoming very marked when the percentage of nickel exceeds 5. The variation of the concentration of carbon in the successive layers of the cementation zone is much more regular for nickel steels than for ordinary carbon steels. The phenomena observed during the slow cooling of nickel steels, cemented so as to exhibit a hypereutectic zone, are qualitatively analogous to those shown by carbon steels subjected to similar treatment, but differ quantitatively from these in two directions: (1) The entity of the liquation phenomena of the cementite is less marked in the case of the nickel steels, and (2) the transition from the hypereutectic to the hypoeutectic zone corresponds with a content of carbon (0.6—0.65%) lower than that (0.9%) of the similar zone for carbon steels.

T. H. P.



**Iron-Chromium Alloys and their Resistance to Acids.** PHILIPP MONNARTZ (*Metallurgie*, 1911, 8, 161—176, 193—201).—Alloys of iron and chromium, free from carbon, may be prepared from chromite by the aluminothermic method. An elaborate apparatus is described by means of which cooling curves of the alloys may be taken immediately the temperature has fallen to 1600°. The fusibility of the slag, and the temperature reached in the reaction, are regulated by the addition of varying quantities of fluorite.

The freezing-point curve has a maximum at about 66% of chromium, corresponding with a compound  $\text{Cr}_2\text{Fe}$  (compare Treitschke and Lammann, *Abstr.*, 1907, ii, 953). The higher the original temperature of the mass, the coarser is the resulting crystalline structure. The alloys are softer than cast iron. Homogeneous castings may be obtained by a special apparatus.

The addition of chromium to iron in the absence of carbon increases the readiness of attack by hydrochloric and sulphuric acids. Concentrated nitric acid renders the alloys passive. The resistance to dilute nitric acid diminishes from 0 to 4% Cr, increases very rapidly from 4 to 14%, and slowly from 14 to 20%. Alloys containing from 40 to 100% Cr even resist prolonged heating with dilute nitric acid to which 5% of sodium chloride has been added. The maximum passivity occurs at 66% Cr. These alloys also remain perfectly bright in laboratory air and in water. The presence of combined carbon increases the resistance to acids very greatly, but at the same time renders the alloys excessively hard. The resistance to acids is also much increased by molybdenum, which improves the mechanical properties. Titanium, vanadium, and tungsten have a similar influence, whilst manganese hastens the attack by acids. C. H. D.

**Colloidal Ferric Hydroxide.** A. V. DUMANSKI (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 232—233; *J. Russ. Phys. Chem. Soc.*, 1911, 43, 546—553).—A colloidal solution of ferric hydroxide, prepared by addition of ammonium carbonate to ferric chloride solution, and purified by dialysis, was kept for a year, and then filtered through a collodion membrane. The freezing point of the solution which did not pass through the membrane was found to be slightly lower than that of the filtrate, and from the difference it is calculated that the molecular weight of the colloid is 3120. From the density of the colloidal solution, the density of the colloidal particles was found to be 4.704 at 0°. H. M. D.

**Preparation of Chromyl Compounds.** HARRY SHIPLEY FRY (*J. Amer. Chem. Soc.*, 1911, 33, 697—703).—This work was undertaken with the object of obtaining chromyl bromide and iodide. These salts cannot be prepared by the interaction of the halide and dichromate of a metal in presence of sulphuric acid, owing to the oxidation of the hydrobromic and hydriodic acids by the chromic and sulphuric acids.

When anhydrous potassium chromate is heated with acetyl chloride and a little glacial acetic acid in presence of carbon disulphide, the mixture becomes dark red. On filtering the product, the filtrate is found to contain a small quantity of chromyl chloride, whilst the residue consists almost entirely of potassium chromate coated with a

brown substance, the formation of which prevents the reaction from proceeding to completion. This brown compound is *chromyl acetate*,  $\text{CrO}_2(\text{OAc})_2$ , and when treated with water is hydrolysed into chromic and acetic acids. It is also produced when a solution of chromyl chloride in carbon tetrachloride is added to silver acetate, suspended in the same liquid, but cannot be separated from the silver chloride which accompanies it.

When dry, powdered chromium trioxide is treated with a solution of acetyl chloride in carbon tetrachloride, and a few drops of glacial acetic acid are added, chromyl chloride is obtained in a yield of 82.43% of the theoretical, together with small quantities of chromic acetate and chloride. The oxychloride cannot be separated from the carbon tetrachloride by fractional distillation.

If chromium trioxide is treated with acetyl bromide under similar conditions, an intense permanganate-red coloration is produced, which rapidly changes to reddish-brown. The latter colour is due to bromine, and the former to an unstable chromyl bromide. The production of the permanganate-red colour is recommended as a test for traces of chromium, and is capable of detecting 0.01 mg. per 1 c.c. of solvent.

On treating chromium trioxide with acetyl iodide, iodine is liberated, but direct evidence is not obtained of the formation of chromyl iodide.

If chromium trioxide is heated with acetic anhydride, and carbon tetrachloride is added to the reaction product, *chromyl acetate* is precipitated as a slightly deliquescent, pale green powder. E. G.

**Chromotellurates.** ARMAND BERG (*Compt. rend.*, 1911, 152, 1587—1589; *Bull. Soc. chim.*, 1911, [iv], 9, 583—585).—On spontaneous evaporation, an aqueous solution containing potassium dichromate (1 mol.), chromium trioxide (2 mols.), and telluric acid (1 mol.) deposits crusts of ill-defined crystals corresponding with the formula  $2\text{K}_2\text{O} \cdot 4\text{CrO}_3 \cdot \text{TeO}_3$ ; *ammonium chromotellurate* closely resembles the *potassium* salt. The *sodium* salt is very soluble and was not obtained pure. The compounds may be regarded as salts of the hypothetical acid  $\text{TeO}(\text{OH})_4$ , of the type  $\text{TeO}(\text{OCrO}_3 \cdot \text{OM})_4$ .

W. O. W.

**Alloys of Molybdenum with Nickel, of Manganese with Thallium, and of Calcium with Magnesium, Thallium, Lead, Copper, and Silver.** N. BAAR (*Zeitsch. anorg. Chem.*, 1911, 70, 352—394).—Alloys of nickel and molybdenum may be prepared by fusing the metals in hydrogen, in crucibles lined with magnesia. The thermal examination has only been carried as far as the alloy containing 70% of molybdenum, as the freezing point of the remaining alloys is above  $1700^\circ$ , that of molybdenum being above  $2100^\circ$ . A single compound is formed, having the composition  $\text{MoNi}$ , and melting with decomposition at  $1340^\circ$ . There is a eutectic point at 49.5% Mo and  $1300^\circ$ , and nickel holds up to 33% of molybdenum in solid solution. Microscopical examination confirms the thermal results.

Liquid manganese and thallium are practically immiscible at  $1200^\circ$ , but the freezing point of manganese is slightly lowered by the addition

of thallium. Manganese is very viscous just above its melting point, and freezing takes place over an indefinite range of temperature.

Alloys of calcium with other metals may be investigated by the thermal method if heated rapidly in hydrogen. Only one cooling curve can be taken with each alloy. The freezing-point curve of mixtures of calcium and magnesium has a simple form, the single compound,  $\text{Ca}_2\text{Mg}_4$ , being indicated by a maximum at  $715^\circ$ , whilst there are eutectic points at  $514^\circ$  and  $446^\circ$ , and 18.7 and 78.7% Ca respectively. Solid solutions are not formed to any appreciable extent. The compound,  $\text{Ca}_2\text{Mg}_4$ , is brittle, silvery in appearance, stable in air, and only slowly acted on by water.

Calcium and thallium form three compounds, of which only one,  $\text{CaTl}$ , is indicated by a maximum on the freezing-point curve, at  $969^\circ$ . A compound,  $\text{Ca}_2\text{Tl}_4$ , is formed at  $555^\circ$ , and another,  $\text{CaTl}_3$ , at  $524^\circ$ . There is a eutectic point at  $692^\circ$  and 38% Ca, and solid solutions are formed to a limited extent, so that the transformation point of thallium is raised by the addition of calcium.

Lead and calcium react together violently in the molten state. The freezing point has maxima at  $649^\circ$  and  $1105^\circ$ , corresponding with the compounds  $\text{CaPb}_3$  and  $\text{Ca}_2\text{Pb}$  respectively. Another compound,  $\text{CaPb}$ , is formed at  $950^\circ$ , and there are eutectic points at  $625^\circ$  and 10% Ca, and at  $701^\circ$  and 58% Ca. All the alloys fall to a black powder in air.

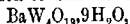
Copper and calcium form only a single compound,  $\text{CaCu}$ , melting at  $933^\circ$ , with eutectic points at 5.7% Ca and  $910^\circ$ , and at 38% Ca and  $560^\circ$ . A thermal change, unaccompanied by change of structure, occurs at  $480^\circ$  in all alloys containing the compound  $\text{CaCu}$ . These alloys are white, and unstable in air.

Silver and calcium form a complicated system, the compounds  $\text{Ag}_3\text{Ca}_2$  and  $\text{AgCa}$  being marked by maxima in the freezing-point curve at  $726^\circ$  and  $665^\circ$  respectively, whilst the compounds  $\text{Ag}_4\text{Ca}$ ,  $\text{Ag}_3\text{Ca}$ , and  $\text{AgCa}_2$  (?) are formed at  $683^\circ$ ,  $595^\circ$ , and  $555^\circ$  respectively. Solid solutions containing  $\text{AgCa}$  and  $\text{AgCa}_2$  undergo a transformation at a lower temperature. All the alloys containing more than 11% Ca decompose water.

The results with alloys of calcium differ in many respects from those of Donsky (Abstr., 1908, ii, 278).

C. H. D.

Iso- and Heteropoly-acids. IV. The Constitution of Metatungstates and Borotungstates. ARTHUR ROSENHEIM (*Zeitsch. anorg. Chem.*, 1911, 70, 418—424. Compare Rosenheim and Kohn, this vol., ii, 116; Copaux, *ibid.*, 402).—The uncertainty of determinations of constitution by dehydration experiments at  $100$ — $120^\circ$  is admitted, but the composition of barium metatungstate,



is considered to be well established. Copaux's views on the borotungstates are also criticised.

C. H. D.

Definite Compounds of Arsenic and Tin. PIERRE JOLIBOIS and EUGÈNE L. DUPUY (*Compt. rend.*, 1911, 152, 1312—1314).—Metallographic evidence has been obtained for the existence of two definite

compounds,  $\text{Sn}_3\text{As}_2$  and  $\text{SnAs}$ . The former is deposited in crystals, D6-31, when an alloy containing 7% of arsenic is employed as anode in the electrolysis of ferrous chloride. Both compounds are attacked by hydrochloric, nitric, and sulphuric acids, and by aqueous solutions of alkalis.

W. O. W.

**Arsenides of Tin.** NICOLA PARRAVANO and PIETRO DE CESARIS (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 593—596).—Investigation of the melting-point diagram of the system arsenic-tin indicates the existence of the compounds  $\text{Sn}_3\text{As}_2$  and  $\text{SnAs}$ .

T. H. P.

**Auric Hydroxide Formed on a Gold Anode.** Department of Auric Hydroxide when Heated. WILLIAM G. MIXTER (*J. Amer. Chem. Soc.*, 1911, 33, 688—697).—The compound formed on a gold anode consists of auric hydroxide with 3 mols. or less of water. When potassium sulphate is used as the electrolyte, the deposit contains potassium, probably present as a potassium hydrogen aurate. If sulphuric acid is employed as the electrolyte, the product contains a little basic auric sulphate which is not removed by cold water. The auric hydroxide deposit is translucent, ruby-red, and appears to be partly crystalline.

When either auric hydroxide from the anode, or the amorphous form obtained by the hydrolysis of auric nitrate or sulphate, is heated, it gradually loses water up to  $172^\circ$ , but does not become anhydrous at  $200$ — $210^\circ$ . At temperatures above  $172^\circ$ , the compound slowly gives off oxygen, but does not yield aurosoauric oxide,  $\text{Au}_2\text{O}_2$ , as stated by Krüss (Abstr., 1887, 15) or auric oxide,  $\text{Au}_2\text{O}_3$ , as indicated by Schottländer (Abstr., 1883, 853).

When auric hydroxide is treated with hydrogen peroxide or a solution of sodium peroxide, it is reduced to the metal.

The deposit formed on a gold anode in presence of ammonium carbonate contains a fulminate.

E. G.

## Mineralogical Chemistry.

**Composition and Occurrence of Rinneite.** FRITZ RINNE and R. KOLB (*Centr. Min.*, 1911, 337—342).—The formula given by H. E. Boeke (Abstr., 1909, ii, 153) for the original rinneite from Wolframshausen was  $\text{FeCl}_2 \cdot 3\text{KCl} \cdot \text{NaCl}$ , but a later analysis by O. Schneider (*Centr. Min.*, 1909, 503) of material from Hildesia, near Hildesheim, showed an excess of sodium chloride; this was, however, explained by the presence of mechanically admixed halite. A new analysis of carefully selected material from Hildesia gave:

Fe.	K.	Na.	Cl.	Mg.	$\text{SO}_4$ .	$\text{H}_2\text{O}$ .
13.57	28.99	5.69	52.02	0.03	0.12	0.02

agreeing with the formula  $\text{FeCl}_2 \cdot 3\text{KCl} \cdot \text{NaCl}$  (the small amounts of magnesium sulphate and water are present as kieserite). Analysis of artificially prepared rhombohedral crystals also lead to the same formula. Rinneite is therefore a triple salt, and not an isomorphous mixture, as would be expressed by the formula  $\text{FeCl}_2 \cdot 4(\text{K}, \text{Na})\text{Cl}$ . The rhombohedral double salts  $\text{CdK}_4\text{Cl}_6$ , etc.,  $\text{MnK}_4\text{Cl}_6$  (chlormanganokalite, Abstr., 1908, ii, 395) are very similar crystallographically to rinneite, but they are regarded as isotypes (of Rinne).

At Wolkramshausen, near Nordhausen in the Harz, rinneite occurs as large, lenticular masses in beds of rock-salt, sylvite, and anhydrite, whilst at Hildesheim, Salzdettfurth, and Riedel, in Hanover, it forms a kieserite-rinneite rock.

L. J. S.

**New Occurrence of Pearceite.** FRANK R. VAN HORN and C. W. COOK (*Amer. J. Sci.*, 1911, [iv], 31, 518—524).—The mineral was found in some abundance in a silver-copper vein in the Veta Rica mine at Sierra Mojada, Coahuila, Mexico; associated minerals are native silver, argentite, proustite, and barytes. It forms aggregates of platy crystals, with a black colour and brilliant metallic lustre; the crystals are twinned, the twin-plane being probably (702). The following analysis agrees with the formula  $8(\text{Ag}, \text{Cu})_2\text{S}_4\text{As}_2\text{S}_8$ , rather than with  $9(\text{Ag}, \text{Cu})_2\text{S}_4\text{As}_2\text{S}_8$  (Abstr., 1896, ii, 658):

S.	As.	Sb.	Ag.	Cu.	Total.	Sp. gr.
17.46	7.56	nil	59.22	15.65	99.89	6.07

L. J. S.

**Mexican Minerals.** HENRI UNGEMACH (*Bull. Soc. franç. Min.*, 1910, 33, 375—409).—Detailed crystallographic descriptions are given of several species, and analyses of the following. Polybasite from I. Las Chiapas, Sonora, and II, from Sonora:

	Ag.	Cu.	Fe.	Zn.	Sb.	As.	S.	Total.
I.	64.49	9.70	0.41	0.34	8.08	1.78	15.10	99.90
II.	68.90	5.21	0.09	—	8.35	1.07	15.33	99.45

Pyromorphite from Cusihiuriacich; crystals, associated with dolomite and hemimorphite, gave:

PbO.	P <sub>2</sub> O <sub>5</sub> .	As <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	CO <sub>2</sub> .	Cl.	Total.
80.85	15.01	1.11	0.58	0.22	not det.	2.57	100.34

L. J. S.

**Parisite, etc., from Granite-pegmatite at Quincy, Massachusetts.** CHARLES PALACHE and CHARLES H. WARREN (*Amer. J. Sci.*, 1911, [iv], 31, 533—557).—The crystallised minerals described are found in the central cavity of pegmatite pipes intersecting the Quincy granite.

*Parisite* occurs as small, clear yellow or amber-coloured crystals of rhombohedral habit ( $c=1.9368$ ); several new crystal-forms are noted. Determinations of the refractive indices by the immersion method gave  $\epsilon=1.757$ ,  $\omega=1.676$  (similar values were obtained for the Colombian

parasite, so that the older determinations of Benarmont appear to be incorrect). Analysis I agrees with the usual formula  $(R''F)_3Ca(CO_3)_3$ . The synchysite from Greenland (Flink, Abstr., 1901, ii, 663) does not differ essentially in its physical characters from parasite, and it is suggested that the excess of calcium carbonate in Flink's formula,  $(R''F)_3Ca_2(CO_3)_4$ , may be due to the presence of admixed calcite. In both minerals the perfect basal cleavage is only seen in altered specimens, the fresh crystals breaking with a conchoidal fracture:

											Total (less O	Sp.
CO <sub>2</sub>	F	CaO	(La,Di)O <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	Gangue. for F)	gr.			
* 24.16	6.56	30.94	27.31	0.32	11.40	0.30	0.20	1.02	99.35	4.320		

\* Also traces of Yt<sub>2</sub>O<sub>3</sub>, SrO, H<sub>2</sub>O.

*Riebeckite* occurs as black, prismatic crystals several cm. in length. The angle between the prism cleavages is 55°5'; the acute negative bisectrix is inclined at 4—5° to *c*, and the plane of the optic axes is perpendicular to (010). The pleochroism is intense. The mineral is always to a greater or less extent intergrown in parallel position with aegirite. Analysis II gives 0.582 Na<sub>3</sub>Fe<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>, 0.834 R<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>, with a slight excess (0.058) of silica. Containing only 42% of the molecule Na<sub>3</sub>Fe<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>, this riebeckite resembles that from Colorado and New Hampshire much more closely than the original riebeckite from Socotra (which contains 68—69%):

												Total (less O
SiO <sub>2</sub>	TiO <sub>2</sub> *	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	F	H <sub>2</sub> O. for F)	Sp. gr.
II. 51.79	1.28	0.68	14.71	31.43	1.15	1.28	0.10	6.16	1.10	0.20	1.30	101.17
III. 51.73	0.64	1.91	31.86	0.37	0.60	0.37	0.14	11.43	0.40	nil.	0.20	100.65

\* Present as ilmenite and anatase.

*Aegirite* forms blackish-green crystals [ $a:b:c = 1.1044:1:0.6043$ ;  $\beta = 73^\circ 27'$ ]. The extinction angle  $a:c = 6^\circ$ . Analysis III agrees closely with the formula  $(R_2', R'')Fe_3Si_4O_{12}$ , and approximates more closely to the theoretical compound Na<sub>3</sub>Fe<sub>2</sub>Si<sub>4</sub>O<sub>12</sub> than any previous analysis of aegirite.

Crystallographic notes are also given of microcline, ilmenite, anatase, fluorite, and wulfenite.

L. J. S.

**Crystallographic Constants of Some Artificial Apatites.**  
 AUGUST DE SCHULTEN (*Compt. rend.*, 1911, 152, 1404—1406).—Crystallographic details are given of the artificial apatities prepared by fusing a tribasic arsenate or phosphate with calcium, strontium, barium or cadmium chloride, or with cadmium bromide. The axis *c* diminishes with the atomic weight of the metal in the calcium, strontium, barium, and lead compounds, or on substituting the halogen for one of higher atomic weight, as in the replacement of fluorine in natural apatite by chlorine. The axis also diminishes when arsenic is replaced by phosphorus.

W. O. W.

**Thomsonite in New Jersey.** FREDERICK A. CANFIELD (*School Mines Quart.*, New York, 1911, 32, 215—216).—White spherical masses with a radially-fibrous internal structure and blades forming

sheaf-like aggregates, found associated with the several zeolites of Bergen Hill, have been previously thought to be epistilbite. The following analysis proves, however, that this material is thomsonite:

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Na <sub>2</sub> O	H <sub>2</sub> O	Total	Sp. gr.
37.90	31.40	12.80	4.53	13.05	99.68	2.35

L. J. S.

**The Olivine Group.** HELGE BACKLUND (*Trav. Muséé Géol. Pierre le Grand. Acad. Sci. St. Pétersbourg*, 1909, 3, 77—105).—The refractive indices and chemical composition of 18 samples of minerals of the olivine group are tabulated, and curves are drawn. Some of these are quoted from other authors, but many of the refractive indices have been newly determined; the following new analyses are given: I, olivine from Windisch-Matrey, Tyrol: asparagus-green, transparent. II, from Kammerbühl, Eger, Bohemia: yellowish to brownish. III, from Vesuvius: dark variety. IV, "glinkite" from Itkul, Urals: large brownish-yellow nodule from talc-schist:

	SiO <sub>2</sub>	MgO	FeO	MnO	Al <sub>2</sub> O <sub>3</sub>	Total	$\alpha$	$\beta$	$\gamma$ (Na)
I.	41.63	51.44	7.36	—	—	100.43	1.6507	1.6689	1.6859
II.	40.09	45.06	14.58	0.21	0.35	100.34	1.6649	1.6830	1.7015
III.	40.35	43.37	16.28	—	0.14	100.14	1.6674	1.6862	1.7033
IV.	38.97	42.29	18.07	0.82	—	99.83*	1.6694	1.6878	1.7057

\* Ni(Co)O, 0.18%.

It is seen that the refractive indices increase progressively with the percentage of iron in the series (Mg,Fe)<sub>2</sub>SiO<sub>4</sub>. Forsterite from the Urals with 0.22% FeO gave  $\alpha=1.6361$ ,  $\beta=1.65185$ ,  $\gamma=1.66975$  (Na); and fayalite from Rockport, Massachusetts, with 68.12% FeO has  $\alpha=1.8236$ ,  $\beta=1.8642$ ,  $\gamma=1.8736$  (Na) (Penfield and Forbes, *Abstr.*, 1896, ii, 373). The determination of the refractive indices of olivines in rock-sections can thus be used as a criterion of the chemical composition, but the determinations of the birefringence and optic axial angle are of no help in this direction. L. J. S.

**The Dokáchi\* Meteoric Stone.** HERBERT E. CLARKE and HERBERT L. BOWMAN (*Min. Mag.*, 1911, 16, 35—46).—In the neighbourhood of the village of Dokáchi, in the Decca district of Bengal, there fell on October 22, 1903, a shower of some hundred meteoric stones, the largest of which weighed 1570.99 grams. Examination of a stone, weighing 17.79 grams, which fell in the village of Rána, showed it to consist of a rather finely granular mixture of olivine and bronzite, with irregular grains of nickel-iron and traces of troilite; some chondrules are present, and the stone is referable to the group of intermediate chondrites (Ci) of Tschermak. Analysis by the methods previously described (*Abstr.*, 1910, ii, 783) gave:

						Silicates.		Total.
						Attacked by HCl.	Unattacked by HCl.	
Nickel-iron.	Magnetite.	Troilite.	Schreibersite.	Chromite.		0.05	37.71	37.93
18.66	1.11	4.10	0.17					99.73

The composition of the nickel-iron alloy is:

Fe.	Ni.	Co.	Cu, Mn, Zn.	Total.
93.5	5.5	1.0	traces	100.0

The silicates attacked by hydrochloric acid gave the results under I, and the unattacked silicates, II:—

	SiO <sub>2</sub> .	FeO.	CaO.	MgO.	Al <sub>2</sub> O <sub>3</sub> .	Cr <sub>2</sub> O <sub>3</sub> .	NiO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	Total.
I.	35.49	37.72	1.48	23.10	0.67	nil	0.26	0.99	0.16	99.87
II.	57.60	14.37	3.51	21.68	0.51	—	0.22	1.23	0.31	99.93

L. J. S.

"Bad Reinerz" in Silesia and its New Medicinal Springs. RUDOLF Woy (*Zeitsch. öffentl. Chem.*, 1911, 17, 181—192).—Exhaustive analyses are given of the water of four new medicinal springs in Reinerz, Silesia. Besides the chemical analyses, the specific conductivities and the lowering of the freezing points have been determined.

The radioactivity of the samples has also been investigated by means of a Mache-Meyer's fontaktometer. As the activity sank to about one-half when the waters were kept for four days in a closed vessel, it is inferred that the radioactivity is due to the presence of radium.

L. DE K.

## Physiological Chemistry.

Excitability of the Respiratory Centre. J. LINDHARD (*J. Physiol.*, 1911, 42, 337—358).—Carbon dioxide is the adequate stimulus for the respiratory centre as pointed out by Haldane; but the excitability of the centre is governed by the tension of the oxygen present, and by a number of different physico-chemical factors. The excitability of the centre, moreover, has for different individuals quite a different value.

W. D. H.

The Effects of Asphyxia on Medullary Centres. I. The Vaso-motor Centre. G. C. MATHISON (*J. Physiol.*, 1911, 42, 283—300).—Lack of oxygen, small doses of carbon dioxide, and intravascular injection of weak organic acids stimulate the vaso-motor centre. In asphyxia, both lack of oxygen and increase of carbon dioxide are factors. Prolonged lack of oxygen, larger doses of carbon dioxide, and repeated injections of acids produce narcosis. Traube waves are seen in lack of oxygen, and administration of carbon dioxide. The results suggest the existence of a common factor, probably the hydrogen ion content of the blood underlying all these actions on nerve-centres.

W. D. H.

Viscosity of Body Fluids. CHARLES D. SNYDER and MARTILLUS H. TODD (*Amer. J. Physiol.*, 1911, 28, 161—166).—The viscosity of blood sera and plasmata increases with fall of temperature, so resembling what is seen with water and other fluids of known com-



position. The temperature-coefficients are greater for the lower ranges of temperature. This variation is in the same direction and of the same character as the variation of the temperature-coefficient of velocities of chemical reactions and of physiological actions.

W. D. H.

**The Meaning of Variation in the Magnitude of Temperature-coefficients of Physiological Processes.** CHARLES D. SNYDER (*Amer. J. Physiol.*, 1911, 28, 167—175).—Variations in the magnitude of temperature-coefficients at various ranges of temperature have been regarded by some writers on physiological processes as being evidence that the phenomena in question cannot be chemical. This assumption is incorrect. Such variations are always seen in all chemical processes.

W. D. H.

**Positive and Negative Phases of Blood-coagulation in Man.** D. A. WELSH (*J. Path. Bact.*, 1911, 15, 467—474).—The positive and negative phases of blood-coagulation are found in certain diseases, associated with cellular disintegration and abnormal increases in leucocytes. They are probably due to liberation of thrombokinase. Thrombi in the heart and pulmonary artery are formed while the blood is in motion; they represent the positive phase, and lead to death. They are analogous to the coagulation produced by injection of nucleo-protein (thrombokinase).

W. D. H.

**Chemical Dynamics of Serum Reactions.** A. G. MCKENDRICK (*Proc. Roy. Soc.*, 1911, B, 83, 493—512).—It is shown that amboceptor and complement are opposed in their action on the cell; in addition, however, the amboceptor acts as a catalyst for the complement. On this basis the expression  $dz/dt = y[(x/cz) - z]/c - [(y/c) - z]^2$  is deduced, where  $y$  = per cent. of amboceptor,  $x$  = per cent. of complement,  $c$  is a constant of dilution,  $z$  is a complex quantity denoting effect (from a chemical point of view, the amounts of  $x$  and  $y$  which have been transformed), and  $t$  is the time.  $(y/c) - z$  denotes the concentration of free amboceptor,  $(x/cz) - z$  the concentration of free complement, and the equation, which was deduced experimentally, indicates that amboceptoral action is bimolecular, complement action unimolecular, and that the former also exerts a catalytic effect. When the substance acted on is present in sufficient quantity, the above equation is applicable to all serum reactions.

It is considered that toxins are of a compound nature, consisting of amboceptor and complement. The action of complement is lytic (hemolytic, bacteriolytic, etc.), that of the amboceptor primarily polymerising or agglutinative.

Owing to the complicated part which amboceptor and complement play in serum reactions, the present system of bacteriolytic and opsonic indices, based on experiments with only one dilution of the serum, is liable to error.

G. S.

**The Mechanism of the Complement Deviation in the Case of Antiprotein Sera.** EDMUND WEIL and WILHELM SPÄT (*Biochem. Zeitsch.*, 1911, 33, 63—72).—The authors draw the conclusion that

there is no anchoring between the antigen and precipitin. The complement-deviation method was employed, and the influence of the antigen-precipitin mixture on the deviation of the complement was compared, when the former substances had been treated with a non-specific adsorbent (coagulated serum-albumin), and when they had not so been treated. It was found that the albumin could adsorb the precipitin both in presence and absence of the antigen, which fact is in contradiction of the Ehrlich theory of a maximal chemical relationship between antigen and precipitin.

S. B. S.

**Anti-agglutination by Extracts of Bacteria.** EDMUND WEILL (*Biochem. Zeitsch.*, 1911, 33, 56—62).—Quantitative investigation of the anti-agglutinating action of bacterial extracts on different immune sera shows that this action is not specific.

S. B. S.

**The Sugar of Plasma and Blood-corpuscles.** RAPHAEL LÉVINE and RAYMOND BOULUD (*Biochem. Zeitsch.* 1911, 32, 287—289).—The authors quote some of their previous publications showing that before Michaelis and Rona and Rona and Döblin (this vol., ii, 302) they had determined the sugar content of blood corpuscles and plasma. They also point out that they had noticed a possible error in determination owing to the setting free of sugar from corpuscles during centrifugalisation of the blood, so that the sum of the sugar in the blood plus the sugar of the plasma is always slightly greater than the sugar of the total blood.

S. B. S.

**Glycolysis. II.** PETER RONA and A. DÖBLIN (*Biochem. Zeitsch.* 1911, 32, 489—508).—Glycolysis (sugar destruction) takes place in the blood when the corpuscles are not hæmolyzed, hæmolysis almost entirely destroying the glycolytic capacity. The greater the ratio of the amount of corpuscles in the amount of sugar, the greater the glycolysis. Experiments carried out in the presence of oxygen, carbon dioxide, and hydrogen showed that even in hydrogen a certain amount of destruction of sugar takes place, and the process does not appear therefore to be, at any rate in the early stages, an oxidative process. In certain cases glycolysis was hastened by the presence of phosphates. When kept the blood loses its glycolytic power; this is also injured by antiseptics. The experiments were carried out with human blood, collected under aseptic precautions.

S. B. S.

**The Maltase of Blood-serum and Liver.** LEONIDAS DOXIADIS (*Biochem. Zeitsch.*, 1911, 32, 410—416).—The serum and liver of different animals contain different quantities of maltase. The action can be increased if the serum or liver extract containing the maltase be neutralised with acid before being allowed to act on maltose. The action is diminished if the liquids containing maltase be warmed to 50° first, but is very appreciably increased, even beyond the action of the simply neutralised preparation, if they are warmed to 50° after neutralisation. It is suggested that this result is due to the acid setting free a weakly-basic substance which is in combination with the maltase.

It was also found that if the maltase preparation is allowed to act on glucose solutions (20—30%), there is a continued increase in the polarisation, suggesting the presence of a synthetic enzyme.

S. B. S.

**Oxydase Properties of Oxyhaemoglobin.** ÉLOI DE STOECKLIN (*Compt. rend.*, 1911, 152, 1516—1518).—Lumière and Chevroliet's experiments (Abstr., 1905, ii, 642) on the oxydase properties of protoplasmic extracts of blood-corpuscles have been repeated and confirmed. These properties appear to be localised in the basic constituents of the extract.

W. O. W.

**Physiology of Lymph. XVI. Local Haemodynamic Action of Tissue Metabolites.** ANTON J. CARLSON, A. WOELFEL, and H. W. POWELL (*Amer. J. Physiol.*, 1911, 28, 176—189).—Extracts of most fresh organs made with Ringer's solution cause vaso-dilatation and fall of arterial blood-pressure. This effect is more marked if the organs used form an external watery secretion. As such organs require more water for their functions, they produce a greater amount of metabolites or hormones, which act as depressor substances. The action decreases with fatigue of the organs (salivary glands); the depressor substance passes in traces into the saliva. The depressor substances are thermostable, and are probably relatively simple materials, such as choline or proteose. They are not acid. The probable mode of action of their metabolites on the blood capillaries is discussed.

W. D. H.

**The Influence of Loss of Blood on Digestive Processes.** N. A. DOBROWOLSKAJA (*Biochem. Zeitsch.*, 1911, 33, 73—104, 105—152).—The experiments were carried out on several dogs with fistulae in different parts of the digestive tract, made by Pawloff's method, and analyses of the secretions through these fistulae were made when the animals received different diets, control experiments being carried out both before and after the removal of the blood from the body. In the latter case one-third to one-half of the total blood was removed. The amounts of the various digestion products and of the enzymes were estimated in the secretions. It was found that the removal of blood caused considerable disturbances both in the secretory and motor functions and in the digestive and absorptive processes. In the secretory and motor functions two stages could be observed, namely, a stage of depression of the secretion, and of the rate of movement of the food; this was followed by a second stage of increased secretion and increased rate of movement of the foodstuffs down the alimentary tract. The secretions in the first stage contained a higher percentage of solid matter. A diminution of the digestive and absorptive functions was noted chiefly in the second stage of the secretory and motor processes. The absence of a diminution in the first stage may be ascribed to the higher concentration of the solids in the secreted juices, and the prolongation of their time of action on the food, owing to the depression of the motor functions. The digestive and absorptive functions are more efficient immediately after the blood-letting if the foodstuff contains larger quantities of

water. Repeated blood-letting causes disturbances of the same character, but more pronounced. An intravenous infusion of physiological saline diminishes somewhat the immediate effect of the blood-letting, but does not exert any marked influence on the subsequent stages of restitution. The effect of the disturbance on the different varieties of foodstuffs (fats, carbohydrates, and proteins) is similar. The restitution of functions after blood-letting takes place at different rates in different parts of the alimentary tract.

S. B. S.

The Rennet Zymogen of the Calf's Stomach. SVEN G. HEDIN (*Zeitsch. physiol. Chem.*, 1911, 72, 187—214).—An infusion of the calf's stomach as nearly neutral as possible contains not only the zymogen of rennin, but also active rennin, which differs somewhat in its properties from rennet obtained by making an extract with hydrochloric acid, the principal difference being that it does not obey the time law of enzymic action. An extract of the zymogen made with dilute ammonia and then neutralised, loses its rennetic power and inhibits the activity of rennet added to it. The inhibitory power resembles that which is exercised by serum. The inhibition disappears and rennetic activity returns when hydrochloric acid is added. The conclusion drawn is that the zymogen consists of rennet in combination with an inhibitory substance; ammonia liberates the latter and destroys the rennet; hydrochloric acid liberates the rennet and destroys the inhibitory substance.

W. D. H.

Antipepsin. I. SERAFINO DEZANI (*Atti R. Accad. Sci. Torino*, 1911, 46, 371—380. Compare Schwarz, *Abstr.*, 1905, ii, 731).—The author describes experiments on the conditions of action of antipepsin.

Gastric mucus of a freshly-killed pig was well stirred up for ten minutes with an equal weight of 0.35% hydrochloric acid, then left to digest for fifty minutes at 50—60°, and filtered. In this way a yellow liquid,  $D_{20}^{25}$  1.010—1.016, was obtained, which gave 1.926—2.360% of solid residue and 0.25—0.32% of ash. It showed the biuret and Millon's reactions, but in most cases it possessed no proteolytic properties. This liquid, which contains no free hydrochloric acid, arrests digestion completely, its antipeptic properties being somewhat diminished by the addition of hydrochloric acid in the proportion present in normal digestive fluids.

About one-fourth part of the ash of the extract consists of calcium phosphate, which exerts a function analogous to that of the co-enzymes, since the dialysed extract exhibits no antiproteolytic properties and regains these partly on addition of the phosphate. But, since the existence of an enzyme which resists boiling cannot be admitted, antipepsin must be regarded as a substance capable of forming, with calcium phosphate, a labile compound which is dissociated on dialysis and re-formed on addition of the original proportion of the salt.

T. H. P.

The Increase of Metabolism Due to the Work of Type-writing. THORNE M. CARPENTER (*J. Biol. Chem.*, 1911, 9, 231—265). From observations on five subjects, it was found that typewriting at the rate of 57—115 words per minute increases the pulse rate from

90—120, and the respiration rate from 19 to 30 per minute. There is a rise of body temperature, and an average rise of 50% in total metabolism. The work done is calculated as 145 kilogram-metres per 1000 strokes of type-writing.

W. D. H.

**Action of Colloidal Sulphur on Sulphur Metabolism. Sulphoconjugation.** LOUIS C. MAILLARD (*Compt. rend.*, 1911, 152, 1583—1586).—Colloidal sulphur, prepared by the interaction of hydrogen sulphide and sulphur dioxide, is completely and rapidly absorbed by rabbits when introduced into the oesophagus. Within twenty-four hours somewhat less than half is eliminated in the urine as mineral sulphates, and a portion in the form of organic sulphates. The normal amount of the latter is increased by 5—13% after the ingestion of sulphur, but the proportion falls below normal when this is withdrawn from the diet. About half of the sulphur is excreted in an incompletely oxidised condition, probably in organic combination, since no sulphur, hydrogen sulphide, or sulphur dioxide is formed on treating the urine with acid. It may be supposed that substances are formed by the conjugation of compounds of the type  $R \cdot SO_2 \cdot OH$  with phenols, and that more highly oxidised compounds escape combination in this way.

W. O. W.

**Calcium Metabolism. II. The Calcium Content of Human Blood After Oral Administration of Large Doses of Calcium.** N. VOORHOEVE (*Biochem. Zeitsch.*, 1911, 32, 394—409).—The method of estimation employed was that devised by the author. It was found that by the daily administration of 2727 mg. of calcium oxide *per os*, either in the form of lactate or chloride, the calcium content of the blood can be increased in the adult or nearly adult man on a calcium rich diet. Under the same conditions, 545 mg. of calcium oxide caused no very appreciable increase. The increase in the calcium content of the blood can be continued for weeks, without any deleterious effects, and continues even for a period after cessation of medication. No decrease of the calcium content could be detected after administration of extra quantities of calcium salts.

S. B. S.

**Biochemical Study of Manganese. I. Metabolism of Manganese and the Law of Minimum Regarding Manganese and Iron.** GUIDO M. PICCININI (*Arch. Farm. speriment. Sci.*, 1910, 9, Reprint 20 pp. Compare following abstract).—Manganese occurs in varying quantities in the different tissues of the animal and human organism. It is obtained from the food, but does not disappear when a diet which does not contain it is administered. The addition of manganese to the ordinary diet causes an increase in the iron of the blood, and of the liver and spleen, and in fact the absorption of iron (and probably also its assimilation) is regulated by the quantity of manganese available in the body (law of minimum).

R. V. S.

**Biochemical Study of Manganese. II.** GUIDO M. PICCININI (*Biochim. Terap. speriment.*, 1910, 2, Reprint 10 pp. Compare preceding abstract).—Colloidal manganese augments *in vitro* the available oxygen

of blood, and maintains this increase for some time. It seems also to have the same action *in vivo*. Colloidal manganese retards the death of guinea pigs injected with the minimum lethal dose of diphtheritic toxin.

R. V. S.

**Fat Metabolism in the Absence of the Pancreatic Juice in the Intestine.** B. C. P. JANSEN (*Zeitsch. physiol. Chem.*, 1911, 72, 158—166).—Fat absorption goes on to a relatively high degree if the pancreatic juice is absent, provided that the pancreas or a part of it is still in the body. If this organ is extirpated, the loss of fat in the faeces is greatly increased. Such animals, however, are in a marasmic state.

W. D. H.

**Formic Acid as an Intermediary Substance in the Catabolism of Fatty Acids and Other Substances.** HENRY D. DAKIN and ALFRED J. WAKEMAN (*J. Biol. Chem.*, 1911, 9, 329—330).—Formic acid is a small constituent of normal urine. Since this acid is readily oxidisable, it is fair to conclude that the quantity actually formed in metabolism must exceed that which finally passes out of the body. It was found that the administration to cats of the sodium salts of acetic, propionic, and butyric and other fatty acids leads to a ten to thirty fold increase in the amount of formic acid in the urine. It is thus probable that formic acid is a stage in the catabolism of fatty acids from acetic acid upwards. The relation of carbohydrates and amino-acids to formic acid formation is under investigation.

W. D. H.

**The Esterification Method and its Use in Experiments on Metabolism.** BRUNO O. PRIEBRAM (*Zeitsch. physiol. Chem.*, 1911, 71, 472—478).—Fischer's esterification method is used, not only for determining and separating the amino-acids formed by the hydrolysis of complex proteins, but also for determining whether amino-acids are formed in the stomach and its ducts. For this purpose the product is evaporated under reduced pressure, and then treated with alcohol and hydrogen chloride as recommended by Fischer. It is pointed out that the results thus obtained may frequently lead to wrong conclusions, as proteins, when suspended in absolute alcohol and treated with hydrogen chloride, are decomposed and esters formed. The decomposition is not a process of alcoholysis, but of hydrolysis and subsequent esterification, the hydrolysis being due to the minute traces of water in the alcohol.

In certain experiments on the hydrolysis of gelatin, glycine could not be isolated as its ester, although proline, alanine, phenylalanine, etc., were readily isolated. This was shown to be due to the fact that the glycine was present as its hydrochloride, and had either not been esterified or the ester formed had been subsequently hydrolysed.

J. J. S.

**Relation between the Digestibility and the Retention of Ingested Proteins.** DONALD D. VAN SLYKE and GEORGE F. WHITE (*J. Biol. Chem.*, 1911, 9, 219—229).—A dog was fed once a day and

the urine collected at intervals afterwards; the rate of nitrogen excretion is taken as an index of the rate of intestinal absorption. Addition of starch to the diet decreased the rate of nitrogen metabolism, but had no effect on the completeness of absorption. Nitrogen excretion followed most rapidly after ingestion of cod; then followed beef, tautog (*Tautoga onitis*), eel, weakfish (*Cynoscion regalis*), mussel, salt cod, and periwinkle. Some of the results noted indicate incomplete absorption. The lowest cleavage products appear to be less capable of maintaining nitrogenous equilibrium than the higher cleavage products. There doubtless is an optimum rate of digestion.

W. D. H.

**Digestion of Protein in the Stomach and Intestine of the Dog-fish.** DONALD D. VAN SLYKE and GEORGE F. WHITE (*J. Biol. Chem.*, 1911, 9, 209—217).—The most noticeable difference in digestion between the warm-blooded and cold-blooded carnivora is the time occupied. Meat in the dog is completely digested and absorbed in twelve hours; about six times as long is required in the dog-fish. The stomach in the dog is empty in about five hours; in the dog-fish it is not entirely empty after forty-eight hours. The slowness is related to the lower temperature of the dog-fish. Protein in the dog-fish is only partly peptonised in the stomach; in the intestine cleavage proceeds probably as far as in the dog. Lipolysis occurs rapidly. The presence of large amounts of urea in the bile, as in the blood, appears peculiar to the shark family.

W. D. H.

**Muscular Work and Protein Metabolism.** ANGELO PUGLIESE (*Biochem. Zeitsch.*, 1911, 33, 16—29).—The experiments were carried out on large dogs, in which one leg was tetanised (sometimes with the attachment of a weight to the muscle), and the other remained at rest. Analyses were carried out of the muscular substance, the plasma of the arterial and venous bloods of the two limbs, the samples employed for analysis corresponding as nearly as possible. The samples were taken from the resting limb before tetanisation of the other. Only a very small diminution (0.02 to 0.06%) was found in the total nitrogen of the tetanised limb. A small, but constant, increase of the uncoagulable nitrogen was found both in the arterial and venous plasma; this increase was more marked in the venous plasma. A small, but constant, increase of albumin was found in the arterial plasma, and a diminution in the venous. On the other hand, a small, but constant, decrease of globulin was found in the arterial plasma and an increase in the venous. The increase of the incoagulable and albumin nitrogen and the decrease of the globulin nitrogen in the arterial plasma, on the one hand, and the increase of the coagulable nitrogen and globulin nitrogen and decrease of the albumin nitrogen in the venous plasma on the other, almost compensated one another, that is to say, there is no appreciable change in the total nitrogen of the arterial and venous bloods together owing to tetanisation. The author draws the conclusion that during tetanisation the chief nitrogenous change is the conversion of albumin into globulin, and that the protein does not serve as the main source of energy.

S. B. S.

**Purine Metabolism. VII. Purine Metabolism during Starvation.** VITTORIO SCAFFIDI (*Biochem. Zeitsch.*, 1911, 33, 153—166).—In animals with synthetic uric acid formation (ducks), the uric acid forms the chief product of metabolism (42—53% of the total nitrogen), and its variations, during starvation or under-nutrition, run more or less parallel with those of the total nitrogen, in which respect it is similar to the urea excretion of mammals. The relationship of total nitrogen to uric acid nitrogen does, however, vary to some extent with the conditions of experiment, being 2.27 under normal conditions and 1.89—1.97 during starvation. In the case of animals, in which the uric acid formation is an oxidative process (dogs), the changes of uric acid secretion caused by starvation are small when the animal has been kept for some time before on a purine-free diet. There is, however, a fall of the uric acid during starvation, which does not appear to have any definite relationship to the changes in the total nitrogen.  
S. B. S.

**Purine Metabolism. VIII. The Content in Purine Bases of Various Kinds of Muscular Tissue.** VITTORIO SCAFFIDI (*Biochem. Zeitsch.*, 1911, 33, 247—251).—The different kinds of muscular tissue of one and the same animal do not possess the same purine content. The heart muscle contains the greatest quantity, then come the ordinary striped muscle fibre, and lastly the plain muscular tissue, which contains only about half of that of the other muscles. The heart is richest in the free purine bases (as contrasted with the combined), then come the plain muscles; ordinary striped muscular tissue contains least. The amounts of purine bases are not proportional to the total nitrogen content. In no case was uric acid found.  
S. B. S.

**Rice as a Foodstuff. The Nitrogen and Phosphoric Acid Metabolism with Rice and other Vegetable Foodstuffs as the Chief Source of Nutrition.** HANS ARON and FELIX HOCSON (*Biochem. Zeitsch.*, 1911, 32, 189—203).—The authors give a series of analyses of unmilled rice and milled rice of various grades, and show that unmilled rice contains 0.7—0.8%  $P_2O_5$ , whereas "under-milled" rice contains 0.4—0.6, and over-milled rice 0.15—0.4%. They carried out a series of metabolism experiments on several individuals with rice as the chief article of diet, with the addition of fish, white bread, etc., and determined the nitrogen and phosphoric acid balances. They showed that with rice as the chief article of diet, nitrogen equilibrium could be attained with a nitrogen intake of about 8 grams per 50 kilo. of body-weight, but that not much more than about 30% of the rice nitrogen was absorbed. Somewhat more than 1.65 grams of  $P_2O_5$  per 50 kilo. of body-weight are necessary under the same conditions for phosphoric acid equilibrium. The authors discuss in conclusion the economic food-value of rice in the tropics.  
S. B. S.

**The Regeneration of Proteins in the Mucous Membrane of the Stomach.** P. GLAGOLEFF (*Biochem. Zeit.*, 1911, 32, 222—230).—The experimental methods employed were similar to those used by



the earlier workers on this subject (Glaessner, etc.). It is found that in the symmetrical halves of the mucous membrane of the dog's stomach the albumose and the nitrogenous substances not precipitable by zinc sulphate are symmetrically distributed. The content in these nitrogenous substances, whether from a fasting or a fed dog, is not constant, and is not, therefore, a function of the state of nutrition of the animal. The origin of these nitrogenous substances is therefore, for the present, unknown, and no conclusions as to the question of protein formation in the mucous membrane can be drawn from the quantitative estimation of them. Furthermore, the mucous membrane during incubation, as in Glaessner's experiments, undergoes autolysis.

S. B. S.

**Histo-chemistry of Spermatozoa.** HERMANN STEUDEL (*Zeitsch. physiol. Chem.*, 1911, 72, 305—312).—The isolated heads of the spermatozoa of the salmon after extraction with alcohol and ether consist of protamine nucleate (nucleic acid, 60.5, and protamine, 35.56%). Very similar figures have been obtained by others in the case of other fish-sperm. Nucleic acid was isolated by Neumann's method; it contained in different preparations 20.71% to 20.87% nitrogen and 6.21 to 6.78% phosphorus. These figures are not very different from those of Miescher and of Mathews, except that the phosphorus is somewhat higher than in their experiments. The figures do not, however, come anywhere near what is required for the author's formula for nucleic acid; the possible sources of error are discussed.

W. D. H.

**Notes.** I. Presence of Dextrose and Creatinine in Hen's Egg. II. Contents of a Dermoid Cyst. III. Some Properties of Hæmatin. IV. Estimation of Peptone in the Presence of Albumoses. V. The Estimation of Sulphur in Urine and the Significance of Neutral Sulphur. ERNST SALROWSKI (*Biochem. Zeitsch.*, 1911, 32, 335—361).—I. The author refers to statements of Diamare that egg-white contains dextrose which can be separated by dialysis, and that the egg-white after dialysis and hydrolysis yields another sugar. The former statement is confirmed. The other sugar referred to is glucosamine. An investigation of the egg-yolk also revealed the presence of dextrose (in contradiction to another conclusion of Diamare's), and, in addition, a substance which reduced Fehling's solution even after removal of the glucose by fermentation. Further examination of the aqueous extract of egg-yolk revealed the presence of creatinine, and also possibly that of a further unknown substance.

II. The author gives a preliminary account of a non-saponifiable substance obtained from the cyst, as to the nature of which no definite conclusions could be drawn, owing to lack of material.

III. In addition to the hæmase of Senter, which is contained in the blood, another substance, namely, hæmatin, exists, which can decompose hydrogen peroxide. In the experiments described the hæmatin was prepared by the peptic digestion of blood. The iron

obtained from hæmatin by decomposition with hydrogen peroxide is in the form of a ferrous salt.

IV. The author gives some details for manipulating when the acid zinc sulphate method is employed for separating peptone from albumoses.

V. Controversial.

S. B. S.

The Relationship between the Higher Fatty Acids and Unsaponifiable Substances during Different Stages in the Development of the Organism. A. COSTANTINO (*Biochem. Zeitsch.*, 1911, 32, 473—481).—In four experiments on fetuses of dogs it was found that the ratio of fatty acids to unsaponifiable substances was approximately constant. In a fifth case, when the embryos were in an early stage of development, there was a marked deviation from this constant. The iodine number of the fatty acids from embryos was high. Newly-born offspring from the same mother killed at intervals of twelve days after birth showed a greater increase in the fatty acids than in the unsaponifiable substances; the iodine numbers also showed a decrease with advancing age.

S. B. S.

Hydrolysis of Esters in the Tissues. PETER RONA (*Biochem. Zeitsch.*, 1911, 32, 482—488).—The experiments were carried out on mono- and tri-butylin by measuring the diminution of the surface-tension of the mixtures by the method already described by the author and Michaelis. The maximum hydrolysis is in the kidney tissue, then follow liver and the mucous membrane of the intestine, and then spleen and lungs. The muscles and brain were inactive in the time intervals occupied by the experiments (generally two hours).

S. B. S.

Soluble Ferments of the Brain. AUGUSTIN WROBLEWSKI (*Compt. rend.*, 1911, 152, 1334—1337).—The brains of vertebrates contain a catalase, peroxydase, lipase, and amylase and enzymes capable of hydrolysing arbutin and salol. Negative results were obtained in a search for invertase, inulase, and proteolytic enzymes.

W. O. W.

Influence of Various Substances on the Gaseous Interchange of Surviving Frog's Muscle. X. TORSTEN THUNBERG (*Skand. Arch. physiol.*, 1911, 25, 37—54).—Battelli and Stern found that the gaseous exchange in tissues is lessened by previous extraction with water, and this is restored by again adding the aqueous extract. The substance responsible for this they named *pnein*. It is now shown that treatment with 1.5% dipotassium hydrogen phosphate solution also causes an increase in the exchange in extracted tissue. Various neutral salts of organic acids (succinic, oxalic, malonic, citric, malic, etc.) elevate the exchange, especially as regards the carbon dioxide given out; their action occurs whether the muscles have been previously extracted or not. Dextrose, sodium acetate, and salts of maleic acid produce no restitution effect on extracted muscles.

W. D. H.

**Muscular Work and its Relation to Ketone Formation.** LUIGI PRETI (*Biochem. Zeitsch.*, 1911, 32, 231—234).—Both in dog and man an increase in the output of acetone substances in the urine was observed after muscular work.  
S. B. S.

**Rôle of Potassium Salts in Frog's Muscles.** W. BURRIDGE (*J. Physiol.*, 1911, 42, 359—382).—Shortening of frog's muscle produced by lactic acid occurs in two stages: (1) a surface shortening, and (2) a deep shortening. Other acids, alcohol, chloroform, nicotine, and bile act similarly with minor differences in some cases. The action of acids is regarded as a direct one on the contractile substance. The shortening produced by potassium salts is probably produced indirectly. Muscles rendered inexcitable by tetanisation or by alcohol still shorten with appropriate concentrations of potassium salts and lactic acid. Persistent contraction is also produced in cardiac muscle by high concentrations of potassium salts. The action on muscle of widely differing substances is explained by assuming that they affect the mobilisation of the potassium salts in muscle.  
W. D. H.

**Action of Acids on Skeletal Muscle.** DOROTHY DALE and GEORGE R. MINES (*Proc. physiol. Soc.*, 1911, xxix—xxx; *J. Physiol.*, 42).—Experiments with various acids on frog's muscles indicate that the effects are mainly due to hydrogen ion concentration.  
W. D. H.

**Action of Salts on the Neural and Non-neural Regions of Muscles.** JOHN NEWPORT LANGLEY (*Proc. physiol. Soc.*, 1911, xxiv—xxv; *J. Physiol.*, 42).—Nicotine causes a transient contraction in certain frog-muscles which is confined to the neural region, and this is antagonised by curare. Potassium salts cause a contraction which is not abolished by curare. The "receptive substance" acted on by nicotine and curare is not specially stimulated by salts. Different muscles exhibit such effects in varying degrees.  
W. D. H.

**Intravital Inhibition of Oxidation in the Liver by Narcotics.** GEORG JOANNOVICS and ERNST P. PICK (*Pflüger's Archiv*, 1911, 140, 327—353).—Recent researches have shown the importance of oxidation in the liver, especially in reference to fat metabolism. The question here investigated is whether such oxidations are influenced by such narcotics as ether and chloroform. Dogs were fed on cod liver oil, with and without narcosis, killed later, and their livers examined chemically for fats and lipoids. In every case without narcosis evidence of intense oxidative activity was found in the liver during the course of fat-digestion. Under the influence of ether or chloroform narcosis, this was only present to a small degree, and this condition lasts some time. The amount of lipoids remains constant if the narcotic is given shortly after the meal, and diminishes only after a long interval; thus the fatty acid component of lipoids behaves like that of ordinary fat.  
W. D. H.

**Biological Properties of Glycuronic Acid. I. Amount of Glycuronic Acid Contained in the Organism.** CESARE PADERI (*Arch. Farm. speriment. Sci.*, 1911, 11, Reprint 24 pp.).—Neither blood nor pancreatic extract has any action on glycuronic acid, but an infusion of liver decomposes it in the course of twelve hours at 38°. When injected intravenously or subcutaneously into rabbits, glycuronic acid is rapidly and almost completely excreted unchanged in the urine. The organism will support large amounts when administered by the mouth, especially if the doses are small. The substance does not cause the appearance of acetone or of formic acid in the urine, but the oxalic acid there is increased. The urine also contains possibly saccharic acid, and a reducing substance which, it is suggested, may be gulose. The administration of glycuronic acid, together with toxic doses of camphor or chloral, does not diminish the toxicity of the latter, so that it is improbable that the combined glycuronic acid occurring in urine is preformed.

R. V. S.

**The Degradation of Carbohydrates in the Liver.** JOSEPH WIRTH (*Biochem. Zeitsch.*, 1911, 33, 49—55).—According to earlier investigations of the author and Embden, those substances which are readily oxidised inhibit the formation of the acetone substances from ketogenic compounds when perfused with them through the liver. Gluconic acid and saccharic acid, when perfused with isovaleric and hexanoic acids, which are ketogenic, did not diminish the amount of acetone that is formed by the latter acids alone; on the contrary, the amount of acetone was high. It was found that when gluconic acid and saccharic acid alone were perfused through the liver, acetone was formed in appreciable quantities. These acids are therefore ketogenic. Similar results were obtained with mucic acid. The results obtained were not, however, very constant, and the author suggests there may be alternative methods of degradation of these acids in the body.

S. B. S.

**Relationship between Urea and Ammonium Salts.** ALFRED J. WAKEMAN and HENRY D. DAKIN (*J. Biol. Chem.*, 1911, 9, 327—328).—Many simple chemical reactions in the body are reversible. The liver, as is well known, makes urea from ammonium carbonate or carbamate. Dog's livers were perfused with urea dissolved in a mixture of blood and saline solution. The concentration of urea was varied, but in every case no increase of ammonia at the expense of the urea was found.

W. D. H.

**Formation of Bile-pigment from the Blood. II.** THEODOR BÄUGSCH and S. YOSHIMOTO (*Chem. Zentr.*, 1911, i, 994; from *Zeitsch. exp. Path. Ther.*, 1911, 8, 639—644).—The bile-pigment excreted was determined in the urine, faeces, and bile in animals with an artificial biliary fistula and ligatured bile-duct before and after the injection of hæmin. The increase of biliverdin excreted during the period of injection corresponded very nearly with the amount of hæmin injected, and only small amounts of the latter substance were discovered in the urine. The change of the injected blood-pigment may be represented

by the equation:  $C_{32}H_{32}O_4N_4Fe + 2H_2O - Fe = C_{32}H_{32}O_6N_4$ . The details of the experimental methods are given, the urobilin solutions obtained by the different analytical processes being examined spectrophotometrically.

S. B. S.

**The Influence of Hæmatoporphyrin, Hæmin, and Urobilin on the Formation of Bile-pigments.** III. THEODOR BRUGSCH and K. KAWASHIMA (*Chem. Zentr.*, 1911, i, 995; from *Zeitsch. expt. Path. Ther.*, 1911, 8, 645—648).—The influence of hæmatoporphyrin, and then successively of hæmin and urobilin on the excretion of biliverdin, was determined by the same method as that employed in the previous investigation. It was found that hæmatoporphyrin is not entirely converted into bile-pigment, as part escapes unchanged in the bile. It is questionable whether it is converted into urobilin at all. Both hæmin and urobilin are oxidised to bilirubin and biliverdin.

S. B. S.

**Some Constituents of Suprarenal, Thyroid, and Testis.** ALFRED LOHMANN (*Zeitsch. Biol.*, 1911, 56, 1—31).—In addition to adrenaline, choline is obtainable from the suprarenal body. Choline, prepared from this organ and from the thyroid and testis, and made synthetically, was purified by Modrakowski's method, and was found to produce a fall of blood-pressure, as originally stated by Halliburton and Mott, and confirmed by numerous other observers since. Modrakowski and his colleagues excepted. Large doses of choline exacerbate respiration, and still larger doses stop it. The suprarenal extract also yields neurine, leucine, tyrosine, and certain bases grouped together as the "histidine fraction." From thyroid extract, choline, a "histidine fraction," and a substance not identified were obtained; the last substance yields a crystalline gold compound, and it may be  $\beta$ -aminovaleric acid.

W. D. H.

**Proteins and Protein Cleavage Products in Egyptian Mummies.** EMIL ABDERHALDEN and ARTHUR WEIL (*Zeitsch. physiol. Chem.*, 1911, 72, 15—23).—In previous work it was shown that the muscles of mummies yield amino-acids on hydrolysis. It is now found that aqueous extracts of the same material without hydrolysis contain glycine, alanine, valine, leucine, aspartic acid, glutamic acid, phenylalanine, and proline. Other acids, including diamino-acids, were found after hydrolysis. The aqueous extract without hydrolysis gives the biuret reaction. The fat of the mummies had undergone cleavage.

W. D. H.

**The Precipitation of Proteins.** ALBERT J. J. VANDEVELDE (*Bull. Soc. chim. Belg.*, 1911, 25, 166—173).—The author gives numerical results of the fractional precipitation of proteins of milk, colostrum, ox- and horse-serum, and eggs by various methods, both when fresh and after antiseptic preservation. He gives tables showing the changes they have undergone when kept under these conditions.

S. B. S.

**Original Acidity of Milk.** FRÉD. BORDAS and F. TOUPLAIN (*Compt. rend.*, 1911, 152, 1274—1276; *Ann. Falsif.*, 1911, 4, 297—301).—By treating milk with an alcoholic solution of acetic acid (Abstr., 1905, ii, 49), and determining the acidity of the serum, the coagulum, the casein with associated insoluble salts, and the pure casein, it has been found that the original acidity of milk is identical with, and therefore probably due to, the acidity of the free casein. It follows then that fresh milk cannot contain lactic or tartaric acid. The serum which has been filtered through a Berkefeld filter, and is optically transparent is not acid, whilst if it contains particles visible under the ultra-microscope it is found to be acid towards phenolphthalein. W. O. W.

**Excretion of the Alkali Metals in Purine Diuresis.** JOHANNES BOCK (*Skand. Arch. Physiol.*, 1911, 25, 239—246).—From experiments on rabbits treated with theophylline, the author finds that in purine diuresis the amount of sodium and potassium excreted increases, but not necessarily *pari passu*. In a case of very strong diuresis the sodium in the urine corresponded almost with the proportion in serum, but the amount of potassium was much greater than in serum. These observations cannot be explained on the hypothesis that the diuresis is due to an increased filtration and diminished resorption. R. V. S.

**The Excretion of Ingested Amino-acids in Liver Diseases, and Diseases Involving Disturbed Metabolism.** NIRO MASUDA (*Chem. Zentr.*, 1911, 1, 999; from *Zeitsch. expl. Path. Ther.*, 1911, 8, 629—638).—The Sørensen-Henriques method was employed. When no amino-acids are ingested, the amount of amino-acids excreted depends on the total nitrogen metabolism, and is higher (4—5% of the total nitrogen excreted) with meat diets than on meat-free diets (1—3%). In normal cases, glycine and alanine are excreted to the extent of 25—30% as amino-acids, but higher numbers are obtained in pathological cases, such as in malignant tumours, especially such as implicate the liver (40—50%), and also in non-malignant diseases of the liver (cirrhosis, etc.). High values were also obtained in diseases of metabolism, such as diabetes and gout, although in the latter case they were but little above the normal. S. B. S.

**The Pressor Bases of the Urine. III.** WILLIAM BAIN (*Lancet*, 1911, i, 1409—1411. Compare Abstr., 1910, ii, 528).—The pressor bases are absent from the urine of children, and begin to be excreted about the age of fourteen. A vegetable diet considerably reduces the amount formed. Eggs and fish reduce the quantity to some extent, but if chicken is taken the amount is but little less than is obtained on an ordinary mixed diet containing butcher's meat. The bases are either absent or much reduced in amount in cases of high blood pressure. This is only partly explained by the low dietary which many such patients take; the main explanation is that the bases are retained in the system and produce the rise of arterial pressure. In gouty people with normal blood pressure, the pressor bases are excreted in normal amounts. W. D. H.

Colloids in the Urine. III. Quantity and Conditions of Solubility of the Urinary Colloids in Healthy and Pathological Kidneys. L. LICHTWITZ (*Zeitsch. physiol. Chem.*, 1911, 72, 215—225).—The urinary colloid (non-protein) occurs in the form of a sol, a gel (reversible by heat), and an irreversible precipitate. Diuretin and theocin increase the precipitation, but other circumstances leading to change in solubility are still not clear. Urinary protein is in a coarser form of division than that in the blood-serum. The amount of urinary colloid is independent of the quantity of water. The non-protein colloid is increased in certain pathological conditions of the kidney, and in many cases runs parallel with the amount of protein. In one case of nephritis, the urine contained more protein than the blood-serum.

W. D. H.

Pathogenesis of Hereditary Haemophilia. THOMAS ADDIS (*J. Path. Bact.*, 1911, 15, 427—452).—The blood in "bleeders" is not deficient in fibrinogen; it yields the normal amount of thrombin and thrombokinase, and contains anti-thrombin, prothrombin, and calcium in normal quantities. The defect is that the change of prothrombin into thrombin occupies so long a time, hence blood coagulation is slow.

W. D. H.

The Esterase and Nuclease Content of Serum in Different Forms of Insanity. GIACOMO PIGHINI (*Biochem. Zeitsch.*, 1911, 33, 190—217).—Chiefly of clinical interest.

S. B. S.

Nature of Parathyroid Tetany. ANTON CARLSON and CLARA JACOBSON (*Amer. J. Physiol.*, 1911, 28, 133—160).—The amount of ammonia in the blood of dogs in parathyroid tetany falls within physiological limits. Injections of calcium salts in amounts sufficient to suppress the tetany do not alter the ammonia concentration of the blood. In ammonia tetany, calcium salts have much less inhibiting action. Parathyroid tetany is also arrested by strontium salts, and except in extreme cases by injection of pituitary extract, hypertonic sugar solution, proteoses, and amyl nitrite, by section of the vagi, and by stimulation of the afferent fibres of the vagus. All such measures are temporary palliatives only. Parathyroid transplantation is alone an effective cure. The other methods merely decrease the excitability of nervous tissues, directly or indirectly, by causing partial cerebral anemia.

W. D. H.

The Action of Antimony on Experimental Trypanosome Infection. JULIUS MORGENROTH and ROSENTHAL (*Chem. Zentr.*, 1911, i, 834—835; from *Berlin klin. Woch.*, 1911, 48, No. 2).—The action of tartar emetic on trypanosomes is more rapid and powerful than any other preparation yet tried, as 0.2 c.c. of a solution of 1 in 1000 causes a disappearance of this organism. The acquisition of a noticeable resistance to the drug by repeated treatment was not observed. The authors, with Halberstädter, succeed in getting an antimony-resistant strain, however, by previous treatment with arsacetin. Potassium hexatantalate had no influence on the trypanosome infection.

and exerted no prophylactic action; on the other hand, it protects the organisms against the action of arsacetin and antimony. A secondary action of the tantalum preparation was also noticed. S. B. S.

**Accumulation of Iodine in the Tissues of Tumours.** M. TAKENURA (*Zeitsch. physiol. Chem.*, 1911, 72, 78—92).—After the subcutaneous administration of alkali iodides, the partition of iodine in the organism of the rat and mouse agrees with what O. Loeb (*Arch. exp. Path. Pharm.*, 1907, 56, 320) found in the rabbit. The iodine content of malignant tumours in the mouse and rat is relatively higher. In mouse carcinoma the tumour approaches in this particular the tissues which are richest in iodine (blood and skin), whereas in rat sarcoma the quantity is not so great. W. D. H.

**Action of Tervalent Ions on Living Cells and on Colloidal Systems. II. Simple and Complex Cations.** GEORGE R. MINES (*J. Physiol.*, 1911, 42, 309—331).—Eleven simple trivalent cations (from rare earths) produce diastolic arrest of the frog's heart at a concentration of 0.00001M. Five complex trivalent cations tested scarcely affect the heart in concentrations one hundred times greater. It is not possible to ascribe the physiological action of ions to any one factor (solution-tension, valency, or ionic velocity); one and the same ion may act differently on different tissues by virtue of different characters or groups of characters. Further, two ions which from the point of view of one tissue exhibit constellations of properties which are alike, may present wholly dissimilar aspects toward another tissue. In certain cases, described in full, these actions are closely paralleled in the relations of ions to various colloidal systems. W. D. H.

**Sodium and Potassium Chlorides.** E. BIERNACKI (*Chem. Zentr.*, 1911, i, 995; from *Zeitsch. exp. Path. Ther.*, 1911, 8, 685—694).—Dogs were fed with a daily diet of rice and horse-meat which contained 0.4—0.6 gram of  $K_2O$ , to which were added varying quantities of sodium chloride (1—8 grams). In addition to a certain influence on the nitrogen metabolism, it was noticed that the ingestion of the sodium chloride caused a loss of potassium by the organism. The sodium salt appears therefore to play a rôle in regulating the potassium metabolism, and replacing an excess of potassium. On the other hand, with a diet poor in potassium a large amount of sodium chloride is not permissible, in that it causes a loss of potassium from the organism itself. S. B. S.

**Pharmacological Action of Uranium.** DENNIS E. JACKSON and FRANK C. MANN (*Indiana University Studies*, 1911, 8, 2—15).—Intravenous injections of a solution of sodium uranyl tartrate into dogs did not produce any marked increase in the rate of lymph flow from the thoracic duct. The action of this salt differs from that of the cyanides in that it produces a more pronounced and prolonged rise in blood pressure, and a much smaller action on the respiration. The method by which uranium prevents coagulation of blood appears to be different from that exercised by most other substances, and probably



consists in the formation of a combination between the metal and those proteins of the blood which are essential for the process of coagulation. The addition of thrombokinase, fibrin ferment, or calcium chloride to blood previously treated with sodium uranyl tartrate does not cause clotting to occur. Nor is it possible to bring about coagulation in such blood by precipitating the uranium with sodium phosphate.

Sodium uranyl tartrate differs further in its action from the cyanides, in that it does not form chemical combinations with hæmoglobin and methæmoglobin, whilst it does not produce a similar inhibition of the decomposition of hydrogen peroxide by blood, or of the oxidation of guaiacum tincture by potato extract. W. J. Y.

**The Influence of the Chlorinated Hydrocarbons of the Fatty Series on the Organism.** KARL B. LEHMANN, VAL. BEHR, LEONHARD QUADFLIEG, MARGARETE FRANZ, GEORG HERRMANN, ADOLF [? HEINRICH] KNOBLAUCH, KARL GUNDERMANN, and WÜRTH (*Arch. Hygiene*, 1911, 74, 1—60).—The toxic effects of air mixed with various vapours was investigated by the methods repeatedly employed by Lehmann and his pupils. The toxicity of the chloro-derivatives may be represented as the result of a large number of comparable experiments on cats by the following numbers: Tetrachloromethane 1, perchloroethylene 1·6, trichloroethylene 1·7, dichloroethylene 1·7, chloroform 2·2, pentachloroethane 6·2, tetrachloroethane 9·1. The methane derivatives are more toxic than the ethane derivative; the ethylene derivatives are intermediate in their action between the two. In the three series of hydrocarbons investigated, it was found that the increase in the chlorine substitution caused a decrease in the toxicity. S. B. S.

**The Value of Individual Amino-acids in the Dog's Organism under Various Conditions.** EMIL ABDERHALDEN and JOSEPH MARKWALDER (*Zeitsch. physiol. Chem.*, 1911, 72, 63—77).—It is found that glycine and *D*-alanine behave differently in the dog's organism. If glycine is added to non-nitrogenous material (sucrose, lard), the amount of amino-acids in the urine falls off markedly. The effect of *D*-alanine in this direction is not so great. The administration of *D*-alanine in general leads to less amino-acid in the urine than does that of glycine. W. D. H.

**The Fate of Non-nitrogenous Components of Aromatic Amino-acids in the Normal Body.** AKIKAZU SUWA (*Zeitsch. physiol. Chem.*, 1911, 72, 113—130).—In alcaptonuria the view is held that the aromatic amino-acids (tyrosine and phenylalanine), which are converted into homogentisic acid, lose ammonia, and so are first converted into the corresponding hydroxy-acids; phenylalanine will thus yield phenyl- $\alpha$ -lactic acid, and tyrosine will yield *p*-hydroxy phenyl-lactic acid, as intermediate products; the latter, however, does not yield alcapton, but the ketonic acid (hydroxyphenylpyruvic acid) may possibly do so. It is now shown by experiments on rabbits and men that this ketonic acid is in health better burnt in the body than

the hydroxy-acid, and this is regarded as additional evidence that the ketonic acid is the intermediate substance both in alcaptonuria and in experiments with perfused livers.

W. D. H.

**Glycogenic Property of Dihydroxyacetone.** ST. MOSTOWSKI (*Compt. rend.*, 1911, 152, 1276—1278).—Thirty to sixty grams of dihydroxyacetone were administered to fowls during four or five days, and the amount of glycogen in the liver and muscles determined after killing the animals. Although the muscles contained only traces of glycogen, a considerable quantity had accumulated in the liver; thus, in three cases, 0.98, 2.14, and 3.14 grams were found, whilst the control livers gave only 0.013, 0.043, and 0.297 gram. Practically all the dihydroxyacetone was assimilated; in one experiment only traces of a reducing substance could be detected in the faeces and intestinal contents after the ingestion of 50 grams of the compound. KÜLZ and others have shown that glycogen may be synthesised from glycerol in the organism, and LÜTHJE has demonstrated the production of dextrose from the same substance (*Archiv Klin. Med.*, 80, 151). It appears probable from the present experiments that trioses are formed as intermediate compounds in this transformation.

W. O. W.

**The Fate of Subcutaneously Administered Sucrose in the Animal Body, and its Effects on Protein and Fat Metabolism.** ERNST HEILNER (*Zeitsch. Biol.*, 1911, 56, 75—86).—If large quantities of an aqueous solution of sucrose are given subcutaneously, a small fraction is not excreted, but burnt in the body. The cleavage of the disaccharide is brought about by an enzyme formed *ad hoc*; such enzymes may be termed protective or immunising.

These large doses of sugar produce nephritis and albuminuria. The injection in fasting animals diminishes protein catabolism, not because it "spares" protein, but because the strong solution interferes with the osmotic processes in the body-cells. Fat metabolism, on the other hand, is increased.

W. D. H.

**Chemico-Toxicological Study of Adrenaline.** GIUSEPPE VENTUROLI and GUIDO TARTARINI GALLERANI (*Giorn. Farm. Chim.*, 1911, 60, 97—103).—Adrenaline, when kept in air, is converted into oxyadrenaline, and this is also the only transformation product of adrenaline which the authors could discover in animals poisoned with adrenaline.

The reactions of adrenaline are not given by oxyadrenaline, with the exception of those of Bronardel and Boutmy (blue coloration with ferricyanide and ferric salt) and Jungmann (blue coloration with phosphomolybdic acid and ammonia).

In the systematic examination for alkaloids, the oxyadrenaline accompanies morphine and narsine in the amyl-alcoholic extract of the ammoniacal solution. If the solution of all three is treated with chloroform, these bases are removed, and oxyadrenaline can then be extracted with amyl alcohol.

R. V. S.

**Di-iodotyrosine and its Possible Application in Therapeutics.** ALBERT BERTHELOT (*Compt. rend.*, 1911, 152, 1323—1325. Compare Oswald, this vol. i, 203, 372).—Animals support the intravenous injection of 3:5-di-iodotyrosine without ill effects. Rabbits tolerate doses of 0.4 gram per kilo. of body-weight, and 2.0 grams has been administered in twenty-four hours by intramuscular injection to a human syphilitic without symptoms of iodism becoming manifest.  
W. O. W.

**Pilocarpine.** II. N. WATERMAN (*Zeitsch. physiol. Chem.*, 1911, 72, 131—139).—Repeated injections of pilocarpine produce diuresis and glycosuria. An injection of 10—15 mg. in rabbits raises the percentage of sugar of the blood for the first two hours; it then falls. The glycosuria is due to increased permeability of the kidney to sugar during the diuresis. The prevention of adrenaline-glycosuria by pilocarpine (Falta, Rudinger, and Epstein) may be due to the lessening of diuresis which occurs during the first hour after pilocarpine injection.  
W. D. H.

**Artificial Pyrexia Produced by Tetrahydro- $\beta$ -naphthylamine Hydrochloride.** ADAM BLACK (*Proc. Roy. Soc. Edin.*, 1911, 31, 333—341).—This drug induces a high temperature in rabbits and dogs by acting on the nervous system; its action is antagonised by ether. The rise of temperature is probably due to decreased heat-elimination. The change in nitrogenous metabolism is very small compared with that produced by diphtheria-toxin. It is probably the action of toxins on the tissues, and not the high temperature which modifies protein metabolism.  
W. D. H.

**Physiological Action of *d*- and *l*-Tetrahydroquinadine.** DOROTHY DALE and GEORGE R. MINES (*Proc. physiol. Soc.*, 1911, xxxi—xxxii; *J. Physiol.*, 42).—In producing diastolic arrest of the frog's heart, no difference could be detected in the *d*- and *l*-compounds, but on skeletal muscle shortening and gradual loss of irritability is more rapidly produced by the *l*-compound. As Cushny first pointed out one tissue may differentiate between a pair of optical isomerides, whilst another tissue cannot do so.  
W. D. H.

**Atoxyl.** V. FERDINAND BLUMENTHAL and EMANUEL NAVASART (*Biochem. Zeitsch.*, 1911, 32, 380—393).—Experiments on rats showed that after administration of bromine and iodine atoxyl compounds, considerable quantities of arsenic can be detected in the liver, which is not the case after administration of atoxyl itself. Experiments were also carried out on rabbits to determine the rate of excretion of arsenic in the urine after administration of various organic arsenic compounds. It was excreted most rapidly after hectine, which only contains 17% arsenic; the next most rapid excretion followed after administration of atoxyl; the rate of excretion was about the same after the calcium salt. In the case of the bromine and iodine compounds the excretion is relatively slow. It is also relatively slow after the administration of insoluble compounds (silver or mercury salts).

In the case of soluble compounds the more toxic they are the more slowly is arsenic eliminated. Experiments on the distribution of arsenic in the various organs after injection of soluble compounds did not reveal any great differences, except in the case of the bromine and iodine compounds already referred to. Tumours (rat sarcomas) exhibited a certain slight affinity for arsenic after injection of certain preparations.

S. B. S.

**Biochemical Investigations with Aromatic Mercury Compounds.** WALTHER SCHRAUTH and WALTER SCHÖLLER (*Biochem. Zeitsch.*, 1911, 32, 509—511).—The authors call attention to certain investigations with various organic compounds of mercury which were not quoted by Blumenthal (this vol., ii, 517), especially their own on "Asurol," and those of E. Fischer and von Mering on  $\beta$ -mercuridipropionic acid. They doubt the spirillicidal action of mercury compounds of this character.

S. B. S.

**The Inefficiency of the Suprarenals in Cases of Phosphorus Poisoning.** ERNST NEUBAUER and OTTO PORGES (*Biochem. Zeitsch.*, 1911, 32, 290—307).—It has been observed that in diseases of the suprarenals (Addison's disease), the glycogen is absent in the liver. This happens also in phosphorus poisoning. It seemed possible, therefore, that the failure of glycogen in the liver in cases of phosphorus poisoning is due to the injury to the suprarenals. Histological examination of these glands after phosphorus poisoning (of rabbits) was undertaken, and it was found that, in contrast to normal animals, they had lost their capacity of being stained by chromium; adrenaline was also absent in the glands of the poisoned animals. Adrenaline was then administered to animals before the phosphorus poisoning, and in several of the experiments it was found that the liver of these animals contained glycogen, whereas in the case of those animals which had been poisoned without previous administration of adrenaline, glycogen was absent. The authors explain why, in certain cases, after administration of adrenaline and poisoning, glycogen was also absent.

S. B. S.

**The Antagonistic Action of the Salts of Calcium and Other Alkaline Earths to Potassium Poisoning.** JACQUES LOEB and HARDOLPH WASTENEYS (*Biochem. Zeitsch.*, 1911, 32, 308—322).—Whereas the toxic action of potassium chloride is antagonised by sodium chloride when 15—17 molecules of the latter salt are present to one of the former, 1/30th of a molecule of calcium chloride only is necessary to produce the same effect, and partial antagonism is effected even by 1/300th of a molecule. The limiting concentration for antagonism is not, however, very sharp. Magnesium chloride is capable of acting antagonistically only to a limited extent, and for a short period; strontium chloride acts like calcium chloride, as does to some extent barium chloride, but in this case the salt itself is toxic. The action of the calcium salt is assumed to be due to the fact that it forms an insoluble calcium compound on the surface of the fish, whereas the corresponding potassium and sodium salts are soluble; hence, a small quantity of calcium can

replace relatively much larger quantities of potassium than can sodium. The highest concentration of potassium chloride that can be antagonised by calcium salts is the same as that which can be antagonised by sodium salts, namely, 6.6 c.c.  $m/2$ -potassium chloride in 100 c.c. of the solution. As in previous investigations, *Fundulus* was the animal employed.

S. B. S.

**Lactones as Fish Poisons.** HANS PRIESS (*Ber. Deut. pharm. Ges.*, 1911, 21, 267—270).—A résumé of recent work on the method of action of fish poisons, including that of Kobert (*Abstr.*, 1904, i, 1905), Herzog (*Abstr.*, 1910, i, 121), Fickendey (*Zeit. angew. Chem.*, 1910, 2166), Overton (*Abstr.*, 1897, ii, 337), Ellinger (*Abstr.*, 1908, ii, 1060), and Hanriot (*Abstr.*, 1907, ii, 292, 386). Xanthotoxin (this vol., ii, 646) produces narcosis in carp in solutions containing one part in 100,000, but the fish recover when placed in clean water.

T. A. H.

**The Combination of Tetanus Toxin with Other Substances.** SIEGFRIED LOEWE (*Biochem. Zeitsch.*, 1911, 33, 225—246).—The capacity of the tetanus toxin to combine with other substances is not confined to brain tissue, but can also take place with red blood-corpuscles and bone-marrow. Combining capacity for brain substance is to a great extent lost by heating the latter. It depends to a great extent on the lipid substances, and can be demonstrated with the lipid-containing extracts of the brain. The binding capacity of the grey substance is greater than that of the white, and that of the basal ganglia greater than that of the cortex. In the grey substance are substances of great combining capacity which are different from the cerebroside, and can be extracted by light petroleum. Numerous fatty substances also show a combining capacity for tetanus toxin, especially the higher fatty acids and their salts with the alkali metals.

S. B. S.

## Chemistry of Vegetable Physiology and Agriculture.

**The Relations between the Sugar-Content of Nutrient Media and Nitrogen Metabolism by Bacteria.** KARL ERNEST BOEHMCKE (*Arch. Hygiene*, 1911, 74, 81—109).—The rapidity of decomposition of various nitrogenous substances (peptone, asparagine, etc.) is regulated largely by the presence or absence of other compounds capable of serving as a source of energy. This is especially the case where the amount of nitrogenous substance is small, as in bouillon; dextrose then serves as the chief source of energy, and leads to an economy of nitrogen for metabolic processes.

Specific differences exist in the behaviour of the bacteria tested; such organisms as *Bacillus proteus* and *B. Friedländer* utilise the

sugar less than *B. mesentericus*, *B. alcaligenes*, and *Vibrio Metschnikoff* as a source of energy, and therefore lead to a more vigorous decomposition of the nitrogenous compounds. These differences were more marked in peptone than in asparagine cultures.

H. B. H.

**Lipase Produced by Bacteria.** N. L. SÖHNGEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 13, 1200—1210. Compare this vol., ii, 319).—The nature of the source of carbon and nitrogen is of no importance for the formation of lipase by micro-organisms. For the former, glycerol, dextrose, calcium lactate, or sodium malate may be used, and for the latter, peptone, asparagine, ammonium chloride, or potassium nitrate. The addition of dextrose to cultures inhibits the hydrolysis of fat only when the organisms concerned are able to produce acids therefrom. It was found that the decomposition of fat decreases as the amount of acid rises, and that it ceases entirely when the culture liquid is about *N*/50 acid. This acid limit is the same for the enzymes of *B. Stutzeri*, *B. lipolyticum-α*, *B. lipolyticum-β*, and of *Odium lactis*. Mineral acids are more potent than organic acids. The conclusion is drawn that rancidity of dairy products can only take place when, owing to the action of alkali-producing bacteria and moulds, the acidity of these products falls below the above limit. The effect of the presence of various compounds on the rapidity of change induced by bacterio-lipase was investigated, and it was found that calcium and magnesium salts, sodium glycocholate, and trimethylamine favour the change; sodium and potassium hydroxide, ferric and manganese salts are less active, univalent alcohols retard the process, whilst sugars and glycerol are without effect.

Oxygen and light favour the decomposition of fats by lipase. Fats may be prepared synthetically by the action of bacterio-lipase on oleic acid and glycerol, but the monoglyceride chiefly results.

H. B. H.

**Purification of Sewage by the Soil and by Bacterial Beds.** ACHILLE MÜNTZ and E. LAINE (*Compt. rend.*, 1911, 152, 1204—1208. Compare this vol., ii, 421).—It has been shown by experiments in which large quantities of earth were treated with sewage, that destruction of organic matter by oxidation with loss of gaseous nitrogen takes place to a much smaller extent in the soil than when sewage is purified by bacterial beds. Nitrification in the former case, however, is increased. The loss of nitrogen from the sewage under the conditions employed was 16.36% during purification by soil and 60% after treatment in the septic tanks.

W. O. W.

**Variation and Carbohydrate Metabolism of Bacilli of the Proteus Group.** T. H. GLENN (*Centr. Bakt. Par.*, 1911, i, 58, 481—495).—An account of experiments designed to lead to the production of strains of organisms of the *Proteus* group, which would possess distinctive powers of acid production from dextrose. No essential variations in the acid-producing power of the organisms resulted. It was found that, although *P. vulgaris* does not ferment actose under aerobic conditions, it was possible by means of

cultivations under anaerobic conditions to induce and increase this power. Further investigations showed that the production of indole by *P. vulgaris* and *Bacillus coli* occurs in the presence of peptone solution alone, or with the addition of glycerol, lactose, and starch; dextrose and sucrose inhibit its production. This inhibitive effect only takes place where the organisms are able to ferment the carbohydrate with production of acid. The addition of more than 0.5% lactic acid to the culture medium had a similar effect.

The acid formed by the fermentation of carbohydrates also leads to an inhibition of gelatin liquefaction by members of the *Proteus* group. The liquefaction of gelatin by *B. cloacae* is not affected by the presence of sucrose and dextrose; this is suggestive of the formation of a peptic ferment by *B. cloacae*, and a tryptic ferment by *Proteus vulgaris*.

*P. mirabilis* appears to be an intermediate form between *P. vulgaris* and *P. Zopfii*, and *P. Zenkeri*, and differs only in the intensity, but not in the quality, of its biochemical reactions. H. B. H.

**The Juice of Beer Yeast.** E. KAYSER (*Compt. rend.*, 1911, 152, 1279—1280. Compare this vol., ii, 421; Lebedeff, *ibid.*, i, 248; ii, 519).—The most active zymase preparations have been obtained by allowing beer yeast to remain for thirty-five to forty hours at 25° before macerating with water according to Lebedeff's process. The ferment prepared in this way is activated by salts of manganese in the same way as yeast itself. W. O. W.

**Fermentation with Yeast.** HANS EULER and GUNNAR LUSDEQVIST (*Zeitsch. physiol. Chem.*, 1911, 72, 97—112).—The yeast employed was poor in maltase; nevertheless, it fermented maltose as rapidly as dextrose. The fermentation of dextrose was greatly accelerated by neutralised or by pure monosodium phosphate; that of mannose was not affected. Previous treatment of yeasts with sugar, phosphate, or mixtures of the two substances does not affect their fermenting power. In other yeasts where such treatment has an effect, it is probably not the zymase, but the auxiliary substances which are affected. Those yeasts which do not respond to previous treatment with phosphate contain a high percentage of phosphoric acid. W. D. H.

**Influence of Antiseptics on Yeast Autolysis.** E. NAVASSART (*Zeitsch. physiol. Chem.*, 1911, 72, 151—157).—The influence of various antiseptics on the autolysis of yeast was investigated on the lines of Salkowski's previous work on liver autolysis. Certain differences are stated in detail between the effect of various antiseptics in the two kinds of autolysis and in the enzymes (nuclease, proteolytic enzyme, etc.) concerned. W. D. H.

**The Degradation of Nitrogenous Substances by Yeast.** OSWALD SCHWARZ (*Biochem. Zeitsch.*, 1911, 33, 30—31).—The evolution of carbon dioxide when glycogen, starch, alanine, caseinogen, etc., were treated with yeast took place in the presence of adrenaline. The

latter, however, only acted when added in the form of the tartrate, and not in the form of hydrochloride. The tartaric acid must therefore be regarded as the source of the fermentative energy.

S. B. S.

**Influence of Enzymes on the Respiration of Plants.** S. D. LWOFF (*Bull. Acad. Sci. St. Pétersbourg*, 1911, [vi], 655—678).—Unboiled taka-diastase exerts a marked retarding influence on alcoholic fermentation by hefanol or zymin, but, after boiling, the enzyme stimulates the action of the zymase. On the respiration of the higher plants, either living or dead (*Vicia faba*, wheat seeds), taka-diastase exerts a stimulating action; this action is especially marked with living objects (*Vicia faba*), where anaerobiosis, according to Palladin, initially takes the form of alcoholic fermentation. Thus, it seems that where alcoholic fermentation proceeds alone and is not complicated by oxidation processes, taka-diastase exhibits its maximum destructive activity, whilst, where the fermentation is only the initial phase, and is connected biologically with subsequent oxidation charges, the taka-diastase possesses its maximum stimulating action. Merck's diastase, boiled or unboiled, produces effects opposite to, and of less magnitude than, those of taka-diastase.

Emulsin, which produces the same effects in the boiled as in the unboiled condition, exerts a marked retarding action on alcoholic fermentation brought about by hefanol, and so proceeding apart from respiration. On the respiration occurring in dead organisms, and hence under abnormal conditions, emulsin exhibits a stimulating influence; but on the normal respiration of living higher plants (*Vicia faba*), emulsin has no action.

T. H. P.

**Variations in the Amounts of Single Phosphoric Acid Compounds in Seeds Depending on Conditions of Vegetation.** Mlle. S. LEWONIEWSKI (*Bull. Acad. Sci. Cracov*, 1911, 85—96).—The amounts of total nitrogen, protein nitrogen, total phosphorus, and phosphorus as lecithins, phytin, in proteins, and in inorganic forms were estimated in different varieties of barley grain obtained with different manures. The results show that the variations in the amounts of nitrogen and phosphorus depend chiefly on the conditions of growth. The amount of phosphoric acid in the same variety of barley grown in different places varied from 0.562 to 0.782%, whilst two different varieties grown in the same place contained respectively 0.957 and 0.937%.

The amounts of phosphoric acid in the proteins vary only slightly; the differences in total phosphorus are due mainly to variations in inorganic phosphorus and phytin. With deficient phosphatic manure the phosphorus is chiefly utilised for the production of nucleo-compounds; production of phytin and accumulation of inorganic phosphorus only occur when the plants have abundance of phosphatic manure. The relations of total phosphorus and of phosphorus soluble in 1% acetic acid to total nitrogen vary widely; the former varied between 100:50 and 100:32, and the latter between 100:20 and 100:6.



It is probable that the estimation of phosphorus soluble in 1% acetic acid (inorganic phosphorus + phytin) will afford indications of the amount of available phosphorus in the soil as good or better than those obtained by estimating the relation  $P_2O_5/N$  in the grain.  
N. H. J. M.

**Origin of Carbon Assimilated by Plants.** LOUIS CAILLETET (*Compt. rend.*, 1911, 152, 1215—1217).—Experiments on plants, such as ferns, which flourish in the absence of much light show that these organisms obtain the carbon requisite for development principally from the organic matter of the soil, and to a much smaller extent from carbon dioxide in the atmosphere.  
W. O. W.

**Phenomena of Fermentation are Actions of Digestion. Study of Denitrification in the Vegetable Kingdom.** PIERRE MAZÉ (*Ann. Inst. Pasteur*, 1911, 25, 369—391. Compare this vol., ii, 518).—The experiments, previously referred to, on the reduction of nitrates by seedlings and on the assimilation of nitrites by plants are described.

Peas and maize seeds all germinated in solutions containing 0.5% of sodium nitrite, and most of them in presence of 1%. In stronger solutions peas failed to germinate, whilst some of the maize seeds germinated in presence of 2% of sodium nitrite.

Culture experiments in which maize was grown in presence of 0.05% of sodium nitrite and the usual minerals, gave very unsatisfactory results until the roots reached the calcareous deposit at the bottom of the bottles. The plants then recovered and grew quite normally.  
N. H. J. M.

**Function of Hormones in Regulating Metabolism.** HENRY R. ARMSTRONG and E. FRANKLAND ARMSTRONG (*Annals of Botany*, 1911, 25, 507—519. Compare Abstr., 1910, ii, 883).—When exposed to the action of hormones the leaf of *Aucuba japonica* becomes a rich chocolate-brown black, and ultimately black. In the case of both *Aucuba* and laurel leaves weak solutions of mineral acids, sodium hydroxide and carbonate, and most metallic salts were without action; those substances able to penetrate the leaf membrane were mercuric chloride (but not nitrate or sulphate), cadmium iodide (but not chloride), sodium and potassium fluorides; further, iodine, carbon dioxide, hydrogen sulphide, and ammonia. Acids of the acetic series are more active as their molecular weight increases; the same applies to the corresponding alcohols. Lactic, benzoic and salicylic acid penetrate the leaf. Volatile organic vapours, especially toluene, chloroform, ether, acetone, piperidine, etc., are all very active excitants.

The action of the excitant is to liberate the enzymes of the cell, the amount of reducing sugar is increased, glucosides are hydrolysed, and oxydases rendered active. The interpretation of the action of hormones previously given is extended to the explanation of a variety of manifestations in vegetable and agricultural chemistry; it is supposed that

growth will be stimulated in those cases where hormones are present in the soil.

The physiological significance of glucosides is discussed, and it is suggested that the compound associated with the dextrose may in some cases act simply as a hormone. In cases where a cyanogenetic glucoside disappears as the seed ripens, as in *Linum*, the hydrogen cyanide may hasten ripening. Glucosides in seeds may furnish hormones on germination which stimulate further growth. The explanation is extended to the attack of plants by fungoid growths which secrete hormones.

The primary effect of the hormone is to condition the separation from each other of the successive layers constituting the protoplasmic complex.

E. F. A.

**Formation of Nitrous Acid in the Living Cell.** PIERRE MAZÉ (*Compt. rend.*, 1911, 152, 1624—1627).—The property shown by plant extracts of developing substances capable of liberating iodine from hydrogen iodide is shared by certain micro-organisms which have been isolated from such extracts. Six species, including *sarcinae*, cocci, and aerobic and anaerobic bacilli were found to produce nitrous acid in cultures in ordinary media, but not in those containing reducing substances, such as milk. The reaction is not due to autolysis, or to the presence of a peroxydase. It appears to take place more rapidly in well aerated cultures than in those deprived of air, although the total amount of nitrous acid obtained in the former case is less, owing to further oxidation.

W. O. W.

**Physiological Importance of Manganese and Aluminium in the Vegetable Cell.** JULIUS STOKLASA (*Compt. rend.*, 1911, 152, 1340—1342).—An account of experiments confirming Bertrand's observations on the beneficial effect of manganese on plant development. Nutrient solutions containing 1/1000 of the gram-atomic weight of manganese or aluminium per litre increase the yield of the plant, but if both are present in these proportions, a toxic effect is exerted. The best results were given by solutions containing half the above quantities.

W. O. W.

**Behaviour of Benzyl Alcohol in Plants.** GIACOMO L. CIAMICIAN and CRO RAVENNA (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 392—394. Compare *Abstr.*, 1909, ii, 604).—When maize plants are watered with a solution of benzyl alcohol, mixed with dextrose in order to render the introduction of the alcohol into the plant more active, part of the alcohol is converted into a glucoside-like compound, which has not been obtained crystalline, but is possibly identical with Fischer's benzylglucoside (*Abstr.*, 1894, i, 4).

T. H. P.

**The Function of the Plant Catalases.** W. ZALESKI and ANNA ROSENBERG (*Biochem. Zeitsch.*, 1911, 33, 1—15).—The catalase action under varying conditions was determined by measuring the increase of pressure in a closed apparatus, when the catalase is allowed to act on a given quantity of hydrogen peroxide. More catalase was found in

fresh than in dried plants. Extraction with ether and acetone diminished the catalase content slightly, extraction with ethyl alcohol very considerably, and with methyl alcohol completely. Acids and acid salts inhibited catalase action, either partly or completely, whereas alkalis or alkaline salts increased the action. Various neutral substances, such as arbutin, pyrogallol, resorcinol, and aloin inhibited the action. The amount of catalase during various stages of germination was also determined; in the case of wheat embryos the amount increased to a maximum and then diminished. The exact determination of the amount is difficult, owing to the presence in the seeds of substances which act deleteriously on the catalase. There appears to be some connexion between the catalase content and the respiratory energy, as determined by estimating the catalase content in different plants by the above-mentioned method, and the amount of carbon dioxide evolved per unit of weight of plant per hour. The majority of experiments carried out up to the present indicate that the catalase plays some part in the oxidation processes of the cell.

S. B. S.

**Pentosans in Lower Fungi.** ARTHUR W. DOX and RAY E. NEIDIG (*J. Biol. Chem.*, 1911, 9, 267—269).—Various moulds of the *Aspergillus* and *Penicillium* groups were grown on a medium consisting of sucrose and inorganic salts. Pentosans and furfuraldehyde (derived from them) were subsequently obtained from the cultures. The percentage yield of pentosans varied from 0.86 to 1.17%. It therefore appears that fungus cells have the power of constructing pentosans out of hexoses or their decomposition products. The nature of the pentoses yielded by the pentosans was not determined.

W. D. H.

**Influence of Zinc and Manganese on the Mineral Composition of "*Aspergillus niger*."** GABRIEL BERTRAND and MAURICE JAVILLIER (*Compt. rend.*, 1911, 152, 1337—1340. Compare Abstr., 1908, ii, 124; this vol., ii, 222).—Manganese accumulates to a greater extent in *Aspergillus niger* when zinc is present in the nutrient solution than when it is absent. Both zinc and manganese individually increase the total ash of the organism, but this is still more marked when both metals are present together.

W. O. W.

**Belladonna and Henbane Extracts.** P. W. DANCHEWITT (*Arch. Pharm.*, 1911, 249, 247—253).—The yields of extract obtainable by different methods from (1) the leaves, (2) the whole subaerial portion of belladonna and henbane and the alkaloidal content of these extracts have been determined.

As regards belladonna, it is shown that leaves yield extracts poorer in alkaloid than those from the whole herb, and that the best yield of extract from either source is obtained by extracting the dry material with alcohol, without removing chlorophyll, whilst extracts richest in alkaloids are obtained in like manner from the dry material, chlorophyll being removed in the process of manufacture.

Dry henbane leaves, by extraction with alcohol, yield about the

same amount of extract as is obtained by evaporation of the expressed juice of the fresh green herb, but the former extract is much richer in alkaloids than the latter. The finished extracts should contain 15% of water.

T. A. H.

**Estimation of Pentosans and Methylpentosans in Cereals and in Wood Fungi.** MIGAKU ISHIDA and BERNHARD TOLLENS (*J. Landw.*, 1911, 59, 59—67).—The amounts of (4) pentosans and (5) methylpentosans of (1) maize, (2) wheat, (3) rye, (4) barley, (5) oats, (6) *Polyporus fomentarius*, (7) *P. pinicola*, (8) *P. hirsutus*, (9) *P. fulvus*, and (10) *Daedalea quercina*, were found to be as follows (% in dry matter):—

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
A .....	4.60	6.93	8.41	9.04	12.39	2.58	5.11	4.62	4.10	3.05
B .....	0.94	1.72	1.69	1.96	1.52	1.74	2.21	2.08	1.01	1.17

The estimations were made by Ellett's method, a special reflux apparatus, described with sketch, being employed for the alcohol extraction. The separation of the two phloroglucides is not absolute; the error is, however, only small, and is to some extent diminished by mutual compensation.

N. H. J. M.

**Cotton Wax.** EDMUND KNECHT and JOHN ALLAN (*J. Soc. Dyers*, 1911, 27, 142—146).—By extraction with benzene, Egyptian cotton yielded 0.47%, American cotton 0.55%, and East Indian cotton 0.38% of cotton-wax, which had m. p. 76°, and resembled beeswax in appearance. About 70% of the crude wax was soluble in light petroleum, and this portion (cotton-wax A), as obtained from "sliver" made from Egyptian cotton, had m. p. 66—67°, acid number 44.1, saponification number 84.3, iodine number 28.55, and was partly soluble in alcohol; it had a dull yellow colour, and resembled beeswax in texture and fracture. On saponification, it gave glycerol and 47.5% of "unsaponifiable" matter. The latter contained (1) hydrocarbons, possibly a mixture of  $C_{21}H_{44}$  and  $C_{29}H_{58}$  with unsaturated hydrocarbons; (2) a phytosterol, which furnished an acetyl derivative, m. p. 127.2°, and (3) colourless aliphatic alcohols. The soap formed from fraction A furnished on acidification stearic, palmitic, and cerotic (?) acids.

The portion (cotton-wax B) of the crude wax insoluble in light petroleum but soluble in benzene amounted to 30%, and was a dark green, granular, plastic mass, which had m. p. 68°, acid number 4.03, and saponification number 83.3. On saponification this portion furnished (1) a black, tarry material, soluble in hot benzene; (2) unsaponifiable matter composed of a phytosterol (acetyl derivative, m. p. 122.4°), viscous hydrocarbons, and a brown gummy substance, and (3) acids, including melissic acid (?) and a mixture of solid and liquid fatty acids.

T. A. H.

**Constituents of Derris Species.** WILHELM LENZ (*Arch. Pharm.*, 1911, 249, 298—305. Compare van Sillevoldt, *Abstr.*, 1900, i, 109; Power, *Abstr.*, 1903, ii, 323).—The root of *Derris elliptica* from New Guinea does not contain any alkaloid. It furnished the following

percentages of extract to the solvents named when applied in the order given: light petroleum, 2.1; ether, 8.9; alcohol, 6.8; water, 4.8. The first of these consisted mainly of fat, and the second of fat with a crystalline substance, derrin. The alcoholic extract contained phlobaphens, resin, and a little tannin.

*Derrin* is best extracted from the roots by boiling benzene. It crystallises from alcohol or ether in small, colourless plates, and melts at 158°. It is toxic to fish, and to its action is probably due the use of this material as a fish poison.

*Derris Stuhlmanni* bark from German East Africa gave the following percentages of extract to the solvents named, applied in the order given: light petroleum, 3; ether, 5; alcohol, 2; water, 10.2. The first of these extracts was a colourless, semi-solid fat, and the second a colourless, wax-like mass, m. p. 89–90°, consisting mainly of a wax alcohol. The alcoholic extract contained more of the wax-like substance, but was chiefly resin. The aqueous extract was chiefly gum and sugar. No alkaloid was present.

T. A. H.

**Constituents of *Fagara xanthoxyloides*.** HANS PRIESS (*Ber. Deut. pharm. Ges.*, 1911, 21, 227–267).—The fruit-rind and root-bark of *Fagara xanthoxyloides*, Lam. (*Xanthoxylon senegalense*, D.C.), used in native medicine in the Cameroons have been examined; the first yields a volatile oil and a crystalline lactone, *xanthotoxin*, which is poisonous, whilst the second furnishes a crystalline phytosterol, *fagarol* (compare Giacosa and Monari, *Abstr.*, 1888, 167; Giacosa and Soave *Abstr.*, 1890, 918).

The seeds of *F. xanthoxyloides* contain 31.9% of fixed oil having a pungent, rancid taste.

The rinds of the fruit gave 2.4% of bright yellow, volatile oil, which at –5° deposited from 3–4% of crystalline matter, and after removal of this had  $D^{15}_D$  0.9229,  $[\alpha]^{15}_D$  –1.20°, acid number 2.19, and saponification number 60.7. It contained methyl nonyl ketone, and an unidentified aldehyde (possibly decic aldehyde), decic acid, linalool dipentene, and an unidentified *sesquiterpene*,  $D^{14}_D$  0.9214,  $[\alpha]^{14}_D$  +4°16' which yields a crystalline *hydrochloride*, and gives a greenish coloration with acetic anhydride and sulphuric acid. The oil on saponification yields acetic acid and a mixture of non-volatile, fatty acids; the linalool is partly present as linalyl acetate.

The crystalline substance, *xanthotoxin*, deposited by the oil was isolated in larger quantity along with resin by extracting the fruit rinds freed from volatile oil with alcohol. It crystallises in large rhombic, biaxial needles, has the formula  $C_{12}H_8O_4$ , m. p. 145°, contains one methoxy-group, yields a *mononitro*-derivative, m. p. 230° crystallising in yellow needles, a *dibromide*, m. p. 164°, separating from xylene in crystals, and behaves as a lactone with alkalis. This substance is being further examined by Thoms, who regards it as a coumarin derivative; it resembles picrotoxin in its toxic action on fish.

A benzene extract of the root-bark on treatment with light petroleum deposited *fagarol*,  $C_{30}H_{48}O_6$ , m. p. 127–128°, crystallising in colourless needles, and giving the reactions of phytosterol; it is

probably identical with an unnamed substance isolated by Giacosa and Monari from the same source (*loc. cit.*), and by Eberhardt from *Fagara carolina*.

The paper concludes with an account of the pharmacognosy of *Fagara* and *Xanthoxylon* species, and gives a tabular statement of the constituents of these so far as they are known. T. A. H.

**Diastrases of the Latex of the Japanese Mulberry Tree** (*Broussonetia papyrifera*). C. GERBER (*Compt. rend.*, 1911, 152, 1611—1614).—The sap of the Japanese mulberry tree contains three very active enzymes which are probably concerned in converting reserve materials of the organism into a form suitable for assimilation. Their activity is most marked at the commencement of inflorescence, after which it slowly diminishes until the leaves are fully developed, when it falls more rapidly. The enzymes are lypolytic, amylolytic, and proteolytic respectively. The last named is remarkably stable towards heat, and in experiments on milk had an optimum temperature at 75°; moreover, metallic salts which are toxic to similar ferments have little influence on this one, whilst other salts, normally retarding or indifferent, may even act as activating agents.

W. O. W.

**Investigation of the "Urucuri" Fruit.** I. FRITZ FRANK and GNÄDINGER (*Gummi Zeit.*, 1910, 24, 1328—1329).—The kernels of "urucuri" fruit obtained from the palm *Attalea excelsa* when extracted with chloroform yielded a fat which on saponification furnished a small quantity of butyric acid, large amounts of decolic, octolic, and hexolic acids with traces of lauric and myristic acids; an alkaloid, forming glistening, pearly leaflets decomposing at 287° without fusion, and a ketone (probably of the terpene series), to which the characteristic odour of the kernel is due, were also isolated.

The woody portion of the fruit, on dry distillation, yielded a tar, which on fractionation furnished cerulignol, a phenolic methyl ether,  $C_9H_{12}O_2$ , b. p. 240—241°, and cresol, b. p. 220°; a brown oil consisting principally of methylpyrogallol dimethyl ether was also obtained.

The more volatile products of distillation yielded formaldehyde, acetone, xanthogallol, a compound,  $C_{13}H_4O_6Br_4$ , m. p. 122° (obtained by treating the steam distillate with bromine water), catechol, pyrogallol dimethyl ether (m. p. 52°), with formic, acetic and propionic acids. Attention is drawn to the similarity of composition to beech wood tar.

F. M. G. M.

**A Colloidal Copper Soap as an Anticryptogamic Paste.** V. VERMOREL and E. DANTONY (*Compt. rend.*, 1911, 152, 1263—1265).—Copper is more effective as a fungicide when applied in the form of a colloidal solution than in the state of a powder as usually employed. Such a solution is prepared by adding a 1% solution of copper sulphate to an equal volume of a 4% soap solution free from alkali. The presence of much sodium stearate is a disadvantage. Addition of a stable colloid of the same electrical sign, such as gelatin, renders the solution more stable towards the action of electrolytes. W. O. W.

**Manurial Experiments with Sugar Beet.** J. GRAFTIAN (*Bied. Zentr.*, 1911, 40, 300—302; from *Ann. Gembloux*, 1910, 55).—Experiments are described in which sugar-beet grown on plots,  $2 \times 1.25$  m., was manured with sodium nitrate, ammonium sulphate (both alone and with lime), and cyanamide respectively. The greatest yield of roots (7.41 kilos.) was obtained with sodium nitrate, and the lowest yield (5.67 kilos.) with cyanamide. The yield of leaf and heads was also greatest with sodium nitrate (7.28 kilos.), and was lowest on the plot which received ammonium sulphate and lime. The latter plot, however, produced roots with the highest percentage of sugar (15.1) and the highest amount of sugar (108.42 grams). The results as regards sugar were very similar with sodium nitrate and with ammonium sulphate, whilst with cyanamide the percentage and yield of sugar were only 14.1 and 79.95 grams respectively.

N. H. J. M.

**Manganese in Wine.** ORESTE PRANDI and ANGELO CIVETTA (*Staz. sper. agrar. ital.*, 1911, 44, 66—83).—All the wines examined (twenty-four) were found to contain manganese ( $Mn = 0.53 - 1.65$  per million), the average amount being 0.82 per million. Usually the wines of better quality contain the highest amounts of manganese.

N. H. J. M.

**A New Treatment of Wine.** PHILIPPE MALVEZIN (*Bull. Assoc. Chim. Sucr. Dist.*, 1911, 28, 770—774).—When wine is left in an atmosphere of nitrogen, clarification rapidly takes place, and the wine takes on the clear limpid appearance associated with age. The author shows that, in absence of oxygen, the fermentation and other changes going on all come to an end, the organisms die, and rapidly settle to the bottom. It seems probable that this is the change normally taking place, the oxygen of the air being gradually absorbed, leaving only nitrogen; by this artificial means, however, the normal process can be much hastened. As nitrogen can be obtained commercially, the treatment is quite practicable on a large scale.

E. J. R.

**Presence of Oxalic Acid in Certain Wines.** L. MONNIER (*Ann. Chim. anal.*, 1911, 16, 168—169).—The author calls attention to the presence of oxalic acid (also crystals of potassium and calcium oxalates) in a wine from a locality in the east of France. The reason of its occurrence seems somewhat doubtful.

L. DE K.

**The Greasiness ("Graisie") of Ciders.** E. KAYSER (*Compt. rend.*, 1911, 162, 1422—1424).—The disease affecting ciders is due to an anaerobic bacillus which is capable of fermenting sucrose with production of carbon dioxide, alcohol, lactic and acetic acids, mannitol, and *lævulose*.

W. O. W.

**Effect of Lime and Humus on the Mechanical and Physical Properties of Clay, Loam, and Sandy Soils.** WILL THIERE (*Gekrönt. Preisschr. Univ. Göttingen*, 1910, 145 pp.).—A study of five

different soils showed that the calcium extracted by 4.26% hydrochloric acid is in combination with carbonic acid and colloidal acids, and, in humous sand, also in combination with strong mineral acids. The amount of colloidal calcium compounds is calculated from the difference in the amounts of lime as indicated by the amount of acid used and by the estimation of carbon dioxide.

Addition of lime to soils results in the precipitation of the colloids, and in increasing the permeability and water-holding power of the soil. In the case of humus soils, addition of lime is especially favourable to the activity of bacteria (nitrogen-fixing and nitrifying organisms); decomposition of the humus may become so rapid as to impoverish the soil.

The methods employed in investigating the soluble soil-colloids consist in extracting the soils with water, precipitating with alcohol, dialysis, and filtration. Partial analyses of the original extracts and of the alcohol precipitates, etc., were made.

N. H. J. M.

**Amount of Manganese in Some Italian Soils.** A. CONTINO *Staz. sper. agrar. ital.*, 1911, 44, 51—55. Compare Leclerc, *Compt. rend.*, 1871, 75, 1209.—Analyses of twenty-three soils of various kinds (sandy, volcanic, clay, and calcareous soils) showed that manganese was always present. One soil (calcareous clay) contained only a trace, whilst the amounts of manganese in the others varied from 0.03 to 0.48% (as  $Mn_2O_3$ ). The average amount was 0.17%.

N. H. J. M.

**Fixation of Phosphoric Acid by Organic Matter of the Soil.** AUGUSTE PETIT (*Compt. rend.*, 1911, 152, 1317—1319).—Phosphoric acid or soluble phosphates are fixed by the inorganic constituents of soil and not by the organic substances. When the latter are isolated, they are found to be incapable of removing phosphates from solution. An ordinary garden soil fixes much more phosphoric acid than a surface soil rich in humus, taken from a forest.

W. O. W.

**Ammonia and Nitrate Formation in Soils.** JACOB G. LIPMAN, PERCY E. BROWN, and IRVING L. OWEN (*Centr. Bakt. Par.*, 1911, 30, 156—181. Compare Abstr., 1910, ii, 435).—The production of ammonia from dried blood in a heavy loam with which various amounts of sand were mixed decreased as the amount of sand increased; with large amounts of sand a good deal of ammonia escapes in the free state.

In mixtures of loam and sand (70:30), considerable amounts of ammonia were produced when only 8% of water was present; the maximum amount of ammonia was with 16% of water. Ammonia production was increased by addition of 0.05% of calcium carbonate, and still more by larger amounts up to 0.3%. With 0.5% there was a fall in the amount of ammonia. With calcium carbonate obtained as a by-product in a borax factory, the amount of ammonia produced was somewhat less, owing probably to the boron present. The same calcium carbonate (containing  $B_2O_3 = 2\%$ ) was found to be injurious to barley and vetches.



Mono- and di-calcium phosphates were found to have about the same effect in increasing ammonia production from dried blood added to soil. Tricalcium phosphate was without effect. N. H. J. M.

**Field Trials with Nitrogenous Manures from the Atmosphere.** JAMES HENDRICK (*J. Soc. Chem. Ind.*, 1911, 30, 522—524).—The results of field experiments showed that calcium nitrate and calcium cyanamide are quite comparable with sodium nitrate and ammonium sulphate in their effects on grain crops. On the whole, calcium nitrate gave the best results, probably owing to the soils being deficient in lime.

When calcium cyanamide is stored, the percentage of nitrogen diminishes. This is chiefly due to the increase in weight which the manure undergoes; there is, however, a slight loss of nitrogen as well. When the manure is mixed with superphosphate, the phosphate is, to a great extent, rendered insoluble; the reaction is accompanied by a considerable rise in temperature, but no loss of nitrogen was detected.

Calcium cyanamide may be mixed with basic slag, bone meal, steamed bone flour, and potassium manures without loss in manurial value. N. H. J. M.

**Manurial Value of Calcium Nitrate and Calcium Cyanamide as Compared with Sodium Nitrate and Ammonium Sulphate.** PAUL BAESSLER (*Bied. Zentr.*, 1911, 40, 302—304; from *Jahresh. Versuchsstat. Köslin*, 1909, 23).—Field experiments in which winter rye was grown in slightly peaty, loamy sand without manure and with the four nitrogenous manures. Phosphoric acid was applied in the forms of superphosphate and basic slag respectively, and all the plots received potassium salts.

Similar experiments were made with winter wheat (on heavy loam), barley (on a loam soil), oats, and carrots.

Sodium nitrate produced the highest yields in every case except oats, with which calcium cyanamide (33·8 kilos. of nitrogen per hectare) gave a somewhat better result. On the whole, calcium nitrate gave the next best results after sodium nitrate. With calcium cyanamide the manurial effect was very variable (40 to 103, as compared with sodium nitrate = 100). Ammonium sulphate varied from 74 to 99%.

N. H. J. M.

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## Analytical Chemistry.

**The Simplest Arrangement for Reading Burettes.** JULIUS F. SACHER (*Chem. Zeit.*, 1911, 35, 622—623. Compare this vol., ii, 432).—The author has used, for some years, an arrangement similar to that described by Goetze (this vol., ii, 531). A hair is fastened round a test-tube which will just slide over the burette, and the closed

end of which has been cut off. The position of the meniscus is read off by means of the hair.

The simplest method of all is to put a small mirror at the back of the burette and make the reading when the meniscus coincides with its mirror image. Greater accuracy still can be obtained by making a horizontal mark with a diamond on the mirror; the reading is then taken when the lower edge of the meniscus, the mark on the mirror, and its mirror image are in a line.

T. S. P.

**A Re-fill Burette.** RICHARD VON DER HEIDE (*Chem. Zeit.*, 1911, 35, 568).—At the top of the burette is a two-way stopcock, the one way connecting with a soda-lime tube, and the other with a pear-shaped stoppered vessel fused on to the stopcock. The stock of standard solution is kept in the stoppered vessel, and may be run into the burette as required. The calibration of the burette commences at the two-way stopcock.

T. S. P.

**Improved Rapid Condenser and Extraction Apparatus.** RICHARD VON DER HEIDE (*Chem. Zeit.*, 1911, 35, 531). A double surface condenser is fitted into the Soxhlet apparatus by a ground-glass joint. In the top of the Soxhlet is a glass partition (annexed diagram), so arranged that the liquid used in the extraction drops from the condenser and is collected in the gutter of the partition, to overflow finally through a central hole into the Soxhlet.



If it is desired to collect the liquid coming from the condenser, it is usually necessary to go to some trouble in altering the position of the condenser. To obviate this, the ground-glass joint of the condenser is fitted with a hole which can be brought into direct connexion with a side-tube fused on to the top of the Soxhlet apparatus. When this connexion is made, the condensed liquid runs through the side-tube into a receiver instead of overflowing through the central hole in the partition.

The flask containing the extracting liquid is heated by means of an electric lamp.

T. S. P.

**Sedimentation Tube for Microscopic Analysis.** EMIL SCHWABE (*Chem. Zeit.*, 1911, 35, 577).—A thin glass tube is drawn out to a capillary at one end and sealed. The liquid containing the precipitate in suspension is put into the tube, and the precipitate allowed to settle into the capillary. The top of the tube is then closed with the finger, the tip of the capillary broken off, and the tube then used as a dropping pipette. With precipitates of varying densities, a rough quantitative separation can be carried out.

T. S. P.

**Burette for the Volumetric Estimation of Gaseous Mixtures, Especially of Furnace Gases.** A. GAWALOWSKI (*Zeitsch. anal. Chem.*, 1911, 50, 435—439).—A portable burette is described for use in gas analysis. It is somewhat similar in shape to the Lunge gas burette, but with the following alterations. The cup at the top of the burette is replaced by a stoppered U-tube, by means of which

the various absorbents can be introduced into the burette. The stopper of the burette is so bored that the two limbs of the U-tube can be connected with each other, or each limb separately with the burette, or the burette with the gas reservoir containing the gas to be analysed. The burette has no tap at the bottom, but is cut off flush at the zero mark, the gas being confined in the burette by immersion in a cylinder containing brine.

T. S. P.

**Exact Gas Analysis.** ARTHUR WILHELMI (*Zeitsch. angew. Chem.*, 1911, 24, 870—874).—The author discusses the various methods for determining the constituents of a gaseous mixture, and also the errors which occur in the ordinary methods of taking samples. For the latter purpose it is recommended that a vacuum pipette be used, blank experiments being made to determine the amount of residual air in the exhausted pipette, so that an appropriate correction can be applied.

A full description is given of a new universal gas analysis apparatus, which is so arranged that the absorption and explosion pipettes, etc., are conveniently arranged round a burette, fitted with a specially-designed central tap by means of which rapid connexion can be made between the various parts.

T. S. P.

**Estimation of Chlorides, Chlorates, and Perchlorates in a Mixture of their Salts.** MARQUEYROL (*Ann. Chim. anal.*, 1911, 18, 167—168).—Chlorine present as chloride is estimated as usual. The total chlorine is estimated by fusing a portion of the salts with ten times the weight of a mixture of equal parts of sodium carbonate and potassium nitrate; thus converting the chlorate and perchlorate into chlorides.

For the estimation of the perchlorate alone, advantage is taken of the fact that both chloride and chlorate are converted into nitrate by evaporating twice with nitric acid (D 1.36) on the water-bath. The perchlorate remains unaffected, and is then converted as before into chloride by fusion. The chlorine as chlorate is obtained by difference.

L. DE K.

**Characteristic Reaction of Bromine.** GEORGES DENIGES (*Bull. Soc. chim.*, 1911, [iv], 9, 542—544).—The author has shown that Malaquin's test for strychnine (Abstr., 1910, ii, 165) depends on the formation of a red or reddish-purple coloration when oxidising agents are added to the reduction products of strychnine (this vol., ii, 655, 672). He proposes to use a reduced strychnine solution as a reagent for bromine by means of the characteristic reddish-purple coloration which this halogen gives with reduced strychnine. The absorption spectrum of the colour given by bromine shows a band in the yellow, the more intense zone of which is in the neighbourhood of  $\lambda = 550$ . The red colours given by other oxidising agents, including chlorine, are characterised by two absorption bands in the green, the more intense having  $\lambda = 510$  and the weaker  $\lambda = 495$ .

Reduced brucine gives an olive-green coloration with oxidising agents.

T. A. H.

**Extraction of Bromine and Iodine from Aqueous Solutions by means of Chloroform or Carbon Disulphide.** A. LABAT (*Bull. Soc. chim.*, 1911, [iv], 9, 503—506).—Of the reagents employed in analysis for the liberation of iodine and bromine simultaneously from halogen salts of alkalis in aqueous solution, chlorine is objectionable, since it obscures the presence of iodine, and sodium nitrite is only useful for iodine. Bromides and iodides may occur in such proportions in a solution that one or both may be undiscoverable by the use of such reagents.

When bromine water is added to an aqueous solution of iodine a colourless or pale yellow solution is produced when the quantities of the two halogens present correspond to those required for the compound  $\text{IBr}_3$ , and this solution does not colour chloroform or carbon disulphide if either of these liquids is shaken with it. The detection of iodine in presence of bromine under these conditions is not facilitated by shaking the separated organic liquid with sodium hydrogen carbonate except by the method prescribed by Bourcet (*Thèse*, Paris, 1908), who used sodium nitrite and sulphuric acid for the liberation of the two halogens. In using sodium nitrite no action takes place with bromides unless sufficient sulphuric acid is present. Then nitrosyl bromide is formed, which colours carbon disulphide or chloroform brown. Nitrosyl bromide is destroyed by water or a solution of sodium hydrogen carbonate, and consequently on shaking the coloured organic liquid with either of these, the brown colour disappears and that of iodine becomes apparent if the latter is present.

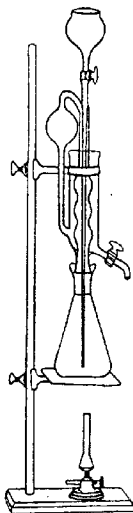
T. A. H.

**Estimation of Total Respiratory Exchange in Man.** C. GORDON DOUGLAS (*Proc. physiol. Soc.*, 1911, xvii—xviii; *J. Physiol.*, 42).—A light and portable apparatus is described, which can be carried in the back, and so expired air can be collected during exercise.

W. D. H.

**Apparatus for the Estimation of Sulphur in Iron or Steel.** D. WENNMANN (*Chem. Zeit.*, 1911, 35, 596).—The apparatus dispenses with the use of rubber connexions and washbottle, and the absorption vessel also serves the purpose of a cooling arrangement. When the flask is removed, the upper part of the apparatus remains in its place.

Five grams of iron or steel borings are placed in the flask, the absorption vessel is filled with 10 c.c. of potassium hydroxide solution (100 grams per litre), and 100 c.c. of dilute hydrochloric acid (1:1) are introduced through the separating funnel, the tap of which is then again closed. The ascending hydrogen sulphide fumes are cooled in the bulbs, pass through the side bulb-tube, and then get absorbed in the alkali. Heat is applied until evolution of gas ceases and the absorption vessel becomes hot; in the case of



steel, however, it is best to wait until it is completely dissolved. Finally, the tap of the separating funnel is turned on, and the alkaline liquid drawn off through the lower tap into a flask. The left side bulb prevents regurgitation of the liquid.

The alkaline solution is acidified with 50 c.c. of dilute sulphuric acid (1 : 3), and to the liquid is added 1 c.c. of starch solution (300 c.c. of water + 10 grams of starch + 200 c.c. of the above potassium hydroxide solution), and the hydrogen sulphide is then titrated with iodine solution (3.91 grams of iodine, 20 grams of potassium iodide + 1000 c.c. of water); 1 c.c. = 0.05% of sulphur.

L. DE K.

**Estimation of Sulphur in Steel and Iron.** ÉMILE JABOULAY (*Rev. gen. chim. pure appl.*, 1910, 12, 190—192).—The author confirms the researches of Corleis, Wolf, and Kinder, who have shown that in this estimation the metal should be rapidly attacked with concentrated hydrochloric acid (D 1.19), and that the evolution of sulphur compounds is largely due to the employment of dilute acid. The paper contains a sketch of apparatus, with detailed description of the author's procedure, in which the hydrogen sulphide evolved is absorbed in a solution of zinc acetate and titrated directly with iodine and thio-sulphate.

F. M. G. M.

**The Estimation of Sulphides in Alkali Cyanide.** EDMUND C. ROSSITER (*J. Soc. Chem. Ind.*, 1911, 30, 583—588).—The author has examined the three methods in use for the estimation of sulphides in alkali cyanide, namely, those of Ewan (*Abstr.*, 1909, ii, 263), Williams (*J. Chem. Metall. Soc. S. Africa*, 1905, 6, 170), and the mercury method as used by the British Cyanides Co. The last method consists essentially in precipitating the sulphide with mercuric chloride solution and collecting and weighing the precipitate obtained, but it is now shown that it cannot be depended on for a greater degree of accuracy than 0.005% of sodium sulphide.

Williams' method may be trusted to within 0.0025% of sodium sulphide when care is taken to insure the formation of the lead sulphide in a colloidal form. Ewan's method is equally accurate when the "personal error" of the operator has been determined, but both these methods are influenced too much by external circumstances, such as the light in the laboratory, individuality of the operator, etc., to be recommended for standard use.

The author recommends the following "powdered lead nitrate method," which is accurate to 0.001% of the sulphide present. The sample of cyanide is tested by the Ewan method, and from the result obtained the quantity of lead nitrate required to precipitate the sulphide in 100 grams of the sample is calculated. One hundred grams of the sample are then treated with about 10% more powdered lead nitrate than is required to precipitate the sulphide and 200 c.c. of air-free water, the mixture being stirred and gently warmed until the solution of the cyanide is complete. A small quantity of the solution is filtered, and tested to prove the presence of excess of lead nitrate; if not present in excess, a fresh sample of cyanide must be treated with a larger quantity of lead nitrate. The excess is then estimated by

adding standard sodium sulphide solution until a small sample of the solution, after filtration, no longer shows lead on testing with sodium sulphide.

If the cyanide contains only 0.015% of sodium sulphide, then 150—200 grams are taken for analysis. The lead nitrate used is finely powdered and dried in a desiccator over sulphuric acid; its purity must be determined before use.

T. S. P.

**Nitrogen Estimations by Kjeldahl's Method.** A. C. ANDERSEN (*Chem. Zentr.*, 1911, i, 1442; from *Skand. Arch. Physiol.*, 1911, 25, 96—104).—Potassium sulphate should not be added unless strictly necessary, as in the case of derivatives of pyridine, piperidine, lysine, etc.; the use of platinum chloride as a catalyst should be avoided, as it causes an appreciable loss in nitrogen. The estimation of the ammonia by formaldehyde titration instead of by distillation cannot be recommended.

L. DE K.

**Improvements in Kjeldahl's Nitrogen Apparatus.** LEO VON LIEBERMANN (*Chem. Zeit.*, 1911, 35, 549).—A small tube provided with a stopcock is fused into the lower end of the distillation tube, and serves to contain a dilute solution of the indicator used in titrating the ammonia. Towards the end of the distillation a few drops are allowed to flow into the tube to test whether the distillation is completed.

E. F. A.

**Estimation of Nitric Oxide.** L. MOSER (*Zeitsch. anal. Chem.*, 1911, 50, 401—433).—See this vol., ii, 598.

**Detection of Nitrates and Nitrites in Water by means of Reduced Strychnine.** GEORGES DENIGES (*Bull. Soc. chim.*, 1911, iv, 9, 544—546).—This is a further application of a solution of the reduction products of strychnine, which as already indicated gives reddish colorations with oxidising agents (this vol., ii, 652, 672). The reagent used is made by adding 5 grams of zinc amalgam to a mixture of 5 c.c. of hydrochloric acid (D 1.18) with 5 c.c. of a 1% solution of strychnine sulphate. This mixture is boiled, cooled, and decanted. With 10 c.c. of water containing 0.0001 gram of nitrous acid per litre, 0.5 c.c. of the reagent gives a red coloration. A coloration is not given by nitrates, except in presence of sulphuric acid, and consequently it is possible to estimate the nitrites colorimetrically first, and then the nitrates, by means of the increase in colour after addition of 5 c.c. of sulphuric acid, comparison being made with that afforded by a nitrite solution of the same strength in nitrates as the water under examination. It is advisable, however, in some cases to eliminate nitrites before testing for nitrates by this reagent, and this may be done by adding to 10 c.c. of the nitrated water 10 drops of ammonia and three or four drops of acetic acid for evaporating to dryness, the treatment being repeated if necessary times

T. P.

**Modification of the Diphenylamine Test for Nitrous and Nitric Acids.** W. A. WITHERS and B. J. RAY (*J. Amer. Chem. Soc.*, 1911, 33, 708—711).—Various methods of preparing the diphenylamine reagent and of applying the test for nitrites and nitrates have been described previously. A study of these has led to a modification of the test which has proved to be very delicate.

The reagent is prepared by dissolving 0.7 gram of diphenylamine in 60 c.c. of concentrated sulphuric acid and 28.8 c.c. of water; after the solution has been well cooled, 11.3 c.c. of hydrochloric acid (D 1.19) are slowly added.

The test is applied as follows: One c.c. of the liquid under examination is placed in a test-tube, one drop of the reagent is added, and the tube is shaken. Concentrated sulphuric acid (2 c.c.) is poured down the side of the test-tube so as to form a layer at the bottom. The tube is now shaken gently in order to cause a slight admixture of the two liquids at the plane of contact, and is then heated at 40° for fifteen to twenty minutes. By this means one part of nitrous nitrogen can be detected in 25 million, or one part of nitric nitrogen in 35 million. By heating for an hour, instead of fifteen to twenty minutes, one part of nitrous nitrogen can be found in 33 million, or one part of nitric nitrogen in 44 million.

E. G.

**The Mechanism of the Partial Disappearance of Phosphorus in the Calcination of Organic Matters, and a Method for Estimating the Ash in those Substances.** ÉMILE FLEURENT and L. LEVI (*Ann. Chim. anal.*, 1911, 16, 125—132, 179—183; *Bull. Assoc. chim. Sucr. Dist.*, 1911, 28, 779—793).—The loss in phosphorus during the burning of animal and vegetable matters is due to the presence of fatty matter, also to the action of carbon and silica at a high temperature. No loss, however, occurs when operating as follows: After removing the fatty matter by suitable solvents, the mass is completely charred in a closed crucible. The char is then moistened with water containing in suspension a known amount of calcium hydroxide (about 0.04—0.15 gram for 10 grams of sample), and the whole is evaporated to dryness. The mass is then transferred to one or several platinum boats, and heated in a combustion tube, first in a current of carbon dioxide, and then in a slow current of oxygen. This way of working also prevents loss of chlorine. When the percentage of ash is required, allowance must be made for the calcium oxide introduced.

L. DE K.

**Volumetric Estimation of Phosphoric Acid Soluble in 2% Citric Acid Solution.** L. WYRYS (*Ann. Chim. anal.*, 1911, 16, 134—137).—Ten c.c. of the citric acid extract (5 grams of the phosphate plus 500 c.c. of 2% citric acid) are mixed with a few drops of hydrochloric acid, and evaporated to dryness in a small, flat porcelain dish. The residue is taken up with 3 or 4 drops of nitric acid and a few c.c. of water, and transferred to a 150 c.c. beaker filtered, of nitric acid (D 1.4) and 15 c.c. of saturated ammonium nitrate not pre-added, and the solution is heated to boiling. After cooling for a larger three minutes, 25 c.c. of molybdate solution are added (90 gram

of ammonium molybdate and a few drops of ammonium in 1 litre). After stirring and waiting for ten minutes, the liquid is decanted through a filter, and the free acid is removed by washing five or six times with cold water. The precipitate is then dissolved in a slight excess of standard potassium hydroxide (326.5 c.c. of *N*-potassium hydroxide to 1 litre), and, after adding 0.5 c.c. of 1% phenolphthalein solution, the excess of alkali is titrated with standard sulphuric acid (1 c.c. = 1 c.c. alkali); 1 c.c. of alkali = 0.001 gram of phosphoric oxide.

L. DE K.

**Physical Properties of Aqueous Solutions containing Ammonia and Citric Acid.** ROBERT A. HALL and JAMES M. BELL (*J. Amer. Chem. Soc.*, 1911, 33, 711—718).—In estimating the "available" phosphoric acid in artificial manures, an "exactly neutral" solution of ammonium citrate is employed. The preparation of this solution is rendered very difficult, owing to the lack of sensitiveness of indicators. A study has therefore been made of some physical properties of mixtures of ammonia and citric acid with a view to applying them to the determination of the end-point, and the results are now given of measurements of conductivity and of density of solutions containing constant amounts of citric acid and varying amounts of ammonia. The curve obtained by plotting the conductivities against the number of c.c. of ammonia solution shows a sharp break at a certain point at which the reagents are present in the proportions required to form triammonium citrate. This indicates the applicability of the conductivity method for determining the point of neutrality. It is also shown that the neutral solution of triammonium citrate has the maximum density. The presence of an excess of ammonia in the ammonium citrate solution can be detected by shaking the solution with chloroform, which dissolves a portion of the excess of the base, but not the free acid or salt.

E. G.

**Detection of Boric Acid in Preservatives.** THEODOR VON ELLENBERG (*Chem. Zentr.*, 1911, i, 1248; from *Mitt Lebens Mittelmeters. Hyg.* 1, 193—194).—One gram of the sample is dissolved in 1 c.c. of hot water, and 1—2 c.c. of strong hydrochloric acid are added. On cooling, boric acid and alkali chloride are deposited; if necessary, a little brine is added. After pouring off the supernatant liquid, the saline mass is boiled with 4—6 c.c. of alcohol, the liquid is decanted, and, after acidifying with sulphuric acid, the alcohol is set light to. The % of borax is thus readily detected.

L. DE K.

**Use of Sodium Paratungstate in the Estimation of Carbon Dioxide in Carbonates and Nitric Pentoxide in Nitrates by Loss on Ignition.** FRANK A. GOOCH and S. B. KUZIRIAN (*Amer. J. Sci.*, 1911, [iv], 31, 497—500).—The carbonates of calcium, strontium, and barium may be readily tested for the actual amount of carbon dioxide by fusing with five times the weight of sodium paratungstate and observing the loss in weight; nitrates may be similarly tested for the amount of nitrogen pentoxide by fusing with three to six times the amount of the flux.



The flux is prepared by fusing over a blast a mixture of equal parts of normal sodium tungstate and tungsten trioxide. The mass is then powdered and is ready for use.

L. DE K.

**Qualitative Analytical Treatment of Silicates with Boric Acid.** ERWIN RUPP and F. LEHMANN (*Chem. Zeit.*, 1911, 35, 546).—Jannasch's method (Abstr., 1896, ii, 219) for the treatment of silicates with boric anhydride in their quantitative analysis is extended to the qualitative analysis of these compounds. One gram of the finely-powdered silicate is intimately mixed with 5—6 grams of crystallised boric acid, and the mixture heated by the blowpipe for twenty-five to thirty minutes in a large platinum crucible. The resulting fusion is dissolved in dilute hydrochloric acid, when at the most only a trace of a sandy residue will be left, which may be neglected. The silica is made insoluble by evaporation to dryness, the residue taken up in warm dilute hydrochloric acid, and the filtrate from the silica treated in the usual manner. It should be noted that in the presence of boric acid the alkaline earths may be partly carried down in the ammonium sulphide group; they may be removed from the precipitate by washing with hot ammonium chloride solution, in which they are soluble.

T. S. P.

**The Titration of Alkali Carbonates in the Presence of Alkali Hydroxides and of Bicarbonates.** J. TILLMANS and O. HREUBLEN (*Zeitsch. angew. Chem.*, 1911, 24, 874—876).—The authors show that the errors which occur in the determination of alkali carbonates in the presence of alkali hydroxides or of hydrogen carbonates according to the ordinary method of titration with an acid, using phenolphthalein and methyl-orange as indicators (compare Küster, Abstr., 1897, ii, 74; Lunge, Abstr., 1897, ii, 285, and Lunge and Lohhöfer, Abstr., 1902, ii, 105), are due to the loss of carbon dioxide, which escapes from the solution without combining with the carbonate to form hydrogen carbonate. The error can be eliminated by carrying out the phenolphthalein titration in a flask, which, after the addition of each lot of acid, is firmly stoppered and well shaken in order that the carbon dioxide may be completely absorbed by the liquid.

Good results may also be obtained by first determining the alkalinity of the solution with methyl-orange as indicator, adding the quantity of acid so determined to a fresh portion of the solution, and then titrating the carbon dioxide set free with sodium hydroxide and phenolphthalein in a stoppered flask, as above. The change from colourless to red is much sharper than the reverse change from red to colourless.

T. S. P.

**Assay of Silver by the Touch Stone.** ALBERT STEINMANN (*Ann. Chim. anal.*, 1911, 16, 165—167).—When applying the touch stone the metallic streak is treated with one or other of the various liquids that have been suggested, and from its action it is possible to judge the percentages of silver actually present.

The following liquid is recommended: 40 c.c. of nitric acid (D 1.37), 50 c.c. of glacial acetic acid, 50 c.c. of water.

It is recommended that the silver ware to be tested should be thoroughly polished; the streaks should be long and powerful, and the acid should be allowed to act until the streak becomes yellowish-brown, when it is instantly removed with a piece of blotting-paper. In the case of alloys containing zinc or cadmium, special comparative tests should be made.

L. DE K.

**Study of the Factors Influencing the Systematic Qualitative Estimation of Barium.** LOUIS J. CURTMAN and EDWARD FRANKEL (*J. Amer. Chem. Soc.*, 1911, 33, 724—733).—In ordinary systematic qualitative analysis it is impossible to detect small quantities of barium (up to 50 mg. in a 1 gram sample) by ammonium carbonate, owing to losses which occur at various stages.

It has been found that in the analysis of a solution containing 100 mg. of barium in 100 c.c., 1.4 mg. are lost in the precipitation of a typical metal of the copper group on account of the oxidation of hydrogen sulphide to sulphuric acid, 14.0 mg. are lost by the action of ferric chloride on hydrogen sulphide, 14.7 mg. are lost owing to the absorption of carbon dioxide during the precipitation of the metals of the iron group with ammonia, 2.2 mg. are lost in the precipitation of a typical metal of the ammonium sulphide group, and 2.8 mg. in the precipitation and filtration of zinc sulphide. Further losses are due to the presence of sulphates in the reagents employed. Moreover, ammonium carbonate fails to detect as much as 10 mg. of barium in presence of ammonium salts.

E. G.

**Estimation of Calcium Oxide in Sugar Refinery Products.** JULIUS WEISBERG (*Bull. Assoc. chim. Sucr. Dist.* 1911, 28, 933—938).—Sidersky's process for the estimation of organically combined calcium oxide in sugar refinery products (*Abstr.*, 1910, ii, 548) is not preferable to the old hydrotimetric process usually employed in the refineries.

L. DE K.

**Schneider's Contribution for the Gravimetric Estimation of Zinc.** RUDOLF GRUND (*Österr. Zeitsch. Berg. Hüttenw.*, 1910, 58, 591—592. Compare *Zeitsch. anal. Chem.*, 1883, 22, 562).—Instead of passing hydrogen sulphide into the diluted neutral solution of a zinc salt, the author recommends that 50—100 c.c. of a concentrated aqueous solution of the gas be carefully poured down the side of the beaker; this forms a zone of zinc sulphide, which is slowly precipitated in large, flocculent masses. Gaseous hydrogen sulphide is then introduced to complete the reaction, and after a period of one to two hours filtration can be effected.

F. M. G. M.

**Estimation of Lead in Alloys Containing Antimony and Tin.** A. G. BLAKELEY and EDWIN M. CHANCE (*J. Soc. Chem. Ind.*, 1911, 30, 518—519).—Briefly, the process is as follows: About 0.5 gram of the alloy is heated with a minimum of aqua regia or hydrochloric acid and potassium chlorate. When nearly dry, the mass is warmed with 5 c.c. of hydrochloric acid and 20 c.c. of water are added, also a few crystals of tartaric acid. Twenty per cent. sodium

hydroxide solution is now added in slight excess, and then 50 c.c. of sodium hydrogen sulphide solution (1:2), when the whole is kept on the boiling water-bath for half an hour. The lead sulphide is then collected and washed with dilute sodium hydrogen sulphide solution (1:100). The filter + contents is now heated in a Jena flask with 25 c.c. of dilute nitric acid (2:3), 20 c.c. of sulphuric acid are added, and the mixture heated until sulphuric fumes appear and the paper is entirely carbonised. After boiling for a few minutes' longer, the contents are allowed to cool slightly, and the carbon is oxidised by adding 0.1—0.2 gram of potassium permanganate and heating again. When cold, the solution, which should be pink or green, is diluted with 50 c.c. of water and heated to boiling, and the excess of permanganate destroyed by means of sulphurous acid. When cold, 25 c.c. of alcohol are added, and the lead sulphate washed, first with 10% sulphuric acid and then once with cold water; it is unnecessary to collect all the sulphate on the filter.

The lead sulphate is dissolved in boiling solution of sodium acetate (90 grams + 8 c.c. of glacial acetic acid per litre), and the solution, which should not be turbid (absence of bismuth), is neutralised with sodium hydroxide with phenolphthalein as indicator, and the pink colour is then again discharged with acetic acid. Ten c.c. of 10% potassium dichromate are added, and the liquid boiled for a few minutes. The lead chromate is washed with hot solution of sodium acetate (50 c.c. of cold saturated solution per litre), and then dissolved in cold dilute hydrochloric acid (1:2). The chromic acid liberated, which represents the lead, is then estimated by adding 2 c.c. of 50% potassium iodide solution and titrating with *N*/10-sodium thiosulphate, with starch as indicator; it is advisable to standardise the thio-sulphate on pure lead foil, using 0.3 gram of the same, and operating as directed.

A slight modification of the process is described for use when a considerable amount of bismuth is present, but below 1% it does not affect the accuracy of the method.

L. DE K.

**A New Method for Determining Copper in Pyrites or Burnt Pyrites.** W. N. IWANOFF (*Chem. Zeit.*, 1911, 35, 531).—Three grams of finely-powdered pyrites or burnt pyrites are intimately mixed with an equal weight of reduced iron, the mixture put into a glass tube, closed at one end and 7 cm. long and 1 cm. diameter, covered with a layer of reduced iron, and heated to a dull red heat for a few minutes. The hot tube is put into a conical flask, cracked by the addition of water, and the mass digested with hydrochloric acid until all the iron has dissolved. The copper is then precipitated with hydrogen sulphide, the precipitate collected, dissolved in nitric acid, and iron, etc., precipitated with ammonium hydroxide. The copper in the filtrate is then determined electrolytically.

It is claimed that the method is more accurate and much more rapid than other methods.

T. S. P.

**Volumetric Estimations of Mercury Based on the Reduction to Metal.** F. REINTHALER (*Chem. Zeit.*, 1911, 35, 593—595).—Of

the various methods proposed, the author prefers that of Feit with a slight modification. The solution, which should contain the metal as mercuric chloride or nitrate, is neutralised as far as possible with sodium hydroxide, and a definite volume of ordinary *N*/10-arsenious acid is added. The whole is then heated on the water-bath in a current of washed carbon dioxide, with frequent shaking, until the reduction to metal is complete, which usually takes from half an hour to an hour and a-half. The deposit should form a fine dark grey, mobile powder without a green shade. When cold, the excess of arsenious acid is titrated as usual with *N*/10-iodine; the mercury now present in numerous globules does not interfere, as it does not act on free iodine for a long time.

L. DE K.

**Analysis of Ferrotitanium Alloys Rich in Silicon.** WOLDEMAR TRAUTMANN (*Zeitsch. angew. Chem.*, 1911, 24, 877).—Ferrotitanium alloys rich in silicon (12%) are not readily taken up by fusion with potassium hydrogen sulphate. One of the two following methods of treatment is recommended: (1) The alloy is roasted in a platinum crucible, the oxides evaporated down once with a few c.c. of hydrofluoric acid, and then submitted to fusion with potassium hydrogen sulphate. The fused mass then dissolves readily in not too dilute hydrochloric acid. (2) The roasted oxides are fused with sodium carbonate and nitrate in a platinum crucible, and the mass dissolved in the crucible with nitric acid. After removal of the crucible, complete solution, with the exception of the silica, is obtained in a few seconds by the addition of hydrochloric acid. Sulphuric acid is then added, and the whole evaporated until fumes appear, after which the residue is warmed with somewhat diluted hydrochloric acid until all the sulphates are dissolved; the solution is made up to a known volume, and the titanium determined in an aliquot portion after filtering off silica and removing any platinum.

The titanium and iron are best determined by Bornemann and Schirmeister's method (this vol., ii, 231). The carbon cannot be determined by direct combustion in oxygen, even when the alloy is mixed with lead peroxide; the alloy must first be treated in a current of chlorine, and then burnt in oxygen. The silicon is determined after taking up the alloy according to the second of the methods described above.

T. S. P.

**Application of the "Glow Reaction" to the Qualitative Detection of the Platinum Metals.** LOUIS J. CURTMAN and P. ROTHBERG (*J. Amer. Chem. Soc.*, 1911, 33, 718—724).—The following method of detecting metals of the platinum group is not so delicate as the potassium iodide test, but is recommended on account of its simplicity and the rapidity with which it can be carried out.

A piece of asbestos paper (about 3 mm. thick) is alternately dipped into the solution under examination and heated, until about 0.2 c.c. has been absorbed. The moist paper is heated to redness in the Bunsen flame, and while still hot is introduced into a mixture of illuminating gas and air issuing from a Bunsen burner. If platinum is present, the paper will glow for some time, and the glow can be

renewed by again heating the paper and holding it in the stream of gas.

The test is sensitive to 0.002 mg. of platinum, 0.0005 mg. of palladium, 0.0009 mg. of rhodium, and 0.005 mg. of iridium, and is not interfered with to any great extent by the presence of other substances. Osmium and ruthenium do not respond to the test, owing, probably, to the volatilisation of the salts of these metals under the conditions of the experiment.

E. G.

**Judging Wines by the Low Alkalinity of the Ash.** W. T. BARAGHOLA and P. HUBER (*Chem. Zentr.*, 1911, i, 1256; from *Mitt. Lebensmittelunters. Hyg.* 1, 158—169).—The authors have arrived at the conclusion that a low alkalinity number of the ash of wines should not be used for judging the quality of the sample unless the cause of the fall is known. It should, therefore, be ascertained whether there is any unusual amount of sulphate or chloride and phosphate present, which, of course, would lower the % of alkalinity in the ash without, however, causing a decreased alkalinity per litre of the wine.

L. DE K.

**Physico-chemical Analysis of Wine According to Dutoit.** E. PHILIPPE and H. DUPERTHUIS (*Chem. Zentr.*, 1911, i, 1255; from *Mitt. Lebensmittelunters. Hyg.* 1, 111—138).—The authors have investigated the physico-chemical process proposed by Dutoit and Duboux (Abstr., 1910, ii, 552), which, except in the case of the alcohol, is based on the determination of the electrical conductivity, and think it offers no particular advantage, except in the estimation of the total acidity, as the neutralisation curve enables one to form a fair idea as to the quality of the sample.

L. DE K.

**Estimation of Alcohol in Wine by means of the Critical Temperature.** H. DUPERTHUIS and E. PHILIPPE (*Chem. Zentr.*, 1911, i, 1255—1256; from *Mitt. Lebensmittelunters. Hyg.* 1, 188—193).—The process given by Duboux and Dutoit (Abstr., 1908, ii, 136) is recommended, the results agreeing with those of the usual specific gravity process. As regards the mixtures employed by those writers, the authors prefer the mixture aniline and alcohol to the mixture nitrobenzene and alcohol.

L. DE K.

**Assay of Sweet Spirits of Nitre.** OTTO HERTING (*Pharm. Zeit.*, 1911, 56, 423).—In a stoppered 100 c.c. flask are placed 10 c.c. of water, 5 c.c. of a saturated solution of potassium chlorate, then 5 c.c. of the sample, and also 5 c.c. of 10% nitric acid. After shaking frequently for thirty minutes, the chloride formed in the reaction is estimated by adding 10 c.c. of *N*/10-silver nitrate and titrating the excess of silver by means of *N*/10-potassium thiocyanate, with iron-alum as indicator. One c.c. of silver solution = 0.0255 gram of ethyl nitrite. If % by weight is desired, the density of the sample should be ascertained.

L. DE K.

**Assay of Sweet Spirits of Nitre.** F. DIETZE (*Pharm. Zeit.*, 1911, 56, 444—445).—A question of priority. The method recommended by Herting, based on the reduction of potassium chlorate

by ethyl nitrite in presence of nitric acid (preceding abstract), was published by the author in 1897 (*Pharm. Zeit.*, 1897, 388), and has also been approved of by other writers.

L. DE K.

**Estimation of Glycerol.** M. WAGENAAR (*Pharm. Weekblad*, 1911, 48, 497—502).—A modification of Muter's process which is based on the solubility of cupric hydroxide in aqueous potassium hydroxide in the presence of glycerol; the copper is then titrated with potassium cyanide.

The author, however, states that the amount of glycerol is not strictly proportional to the cupric hydroxide dissolved, but that this depends on the degree of alkalinity and dilution. The new process is briefly as follows: 50 c.c. of glycerol solution (containing at most 1.2 gram of real glycerol) are placed in a tall stoppered cylinder and 25 c.c. of 4*N*-sodium hydroxide and 25 c.c. of *N*-copper sulphate are added, and the whole is thoroughly shaken. When the excess of cupric hydroxide has settled, 25 c.c. are pipetted off, 5 c.c. of 30% potassium iodide solution and 10 c.c. of 4*N*-sulphuric acid are added, and the copper is titrated with *N*/10-thiosulphate. When testing fats or fatty mixtures, a sufficiency is saponified with *N*/2-alcoholic potassium hydroxide, and then rendered acid with *N*/2-acid to Congo-red. After boiling off the alcohol, the fatty acids are removed by filtration, and the aqueous liquid is made up to 50 c.c. and treated with alkali and copper solution as directed. Reference is now made to an empirical table giving the amount of glycerol corresponding with from 1 to 30 c.c. of thiosulphate. The process may no doubt be applied to other substances having the property of forming alkaline copper solutions, such as sugar, mannitol, tartaric acid, etc. Each of these, of course, requires a separate empirical table.

L. DE K.

**Fehling's Solution.** W. ROSENKRANZ (*Zeitsch. Ver. deut. Zuckerind.*, 1911, 426—434).—The influence of the amount of alkali hydroxide in Fehling solution on the reduction is discussed; further, the effect of boiling the Fehling solution and the sugar under a condenser and so preventing concentration is shown to be considerable. Boiling under a condenser at various pressures has but little effect. The presence of sucrose increases the apparent reduction of invert sugar solutions, both under reduced pressure and at the ordinary pressure. Fehling's solution decomposes at 109.6° at a pressure of 1.4 atmospheres.

E. F. A.

**Jolles's Polarimetric Estimation of Sugars based on the Use of Alkali.** BRUNO BARDACH and SIEGMUND SILBERSTEIN (*Zeitsch. Nahr. Genussm.*, 1911, 21, 540—543).—A slight modification of Jolles's process (this vol., ii, 74).

A measured volume of the sugar solution is diluted with *N*-sodium hydroxide until the alkalinity of the liquid becomes decinormal. The liquid is polarised, a measured quantity introduced into a narrow beaker, and kept for twenty hours without interruption in a thermostat at 36—39°. The solution is then allowed to cool, the original volume is restored, and another polarisation is taken. Defecation

with basic lead acetate is unnecessary. As the polarisation of dextrose is not entirely destroyed, but becomes slightly reversed, the following formulae should be employed. In sucrose-dextrose mixtures the polarisation value ( $D$ ) of the dextrose is found from  $D = A - B - 0.25$ , and the value ( $S$ ) for sucrose from  $S = B + 0.25$ ,  $A$  being the value before and  $B$  the value after the action of the alkali. L. DE K.

**Estimation of Sugar and of Phosphoric Acid.** Preparation of Methylglycuronic Acid. IVAR BANG (*Biochem. Zeitsch.*, 1911, 32, 443—445).—*The Preparation of the Copper Solution in the Author's Sugar Titration Method.*—The thiocyanate is made by first dissolving the carbonate in water, and then adding the other constituents; 166.67 grams of copper sulphate are dissolved in 1 litre of water, and 150 c.c. of this solution are then added to the salt solution.

*Estimation of Phosphoric Acid by Neumann's Method.*—The phosphomolybdate precipitate is dissolved in excess of  $N/2$ -potassium hydroxide solution. Instead of getting rid of the ammonia by heating, it is converted into hexamethylenetetramine by formaldehyde, and the excess of alkali hydroxide can then be estimated by direct titration.

*The Preparation of Methylglycuronic Acid.*—The urine of rabbits, after administration of menthol, is treated with ammonium sulphate to half saturation the mixture heated, and filtered. The ammonium glycuronate separates almost quantitatively on cooling in a pure condition. S. B. S.

**Iodometric Estimation of Sugar in Urine.** ALBERT FERNAU (*Chem. Zentr.*, 1911, i, 1012; from *Zeitsch. Allg. Österr. Apoth. Ver.*, 1911, 49, 85—86).—The urine is diluted if it contains more than 0.8% sugar. The diluted solution is then treated with the two Fehling's solutions (I, copper sulphate; II, Rochelle salt and sodium hydroxide), and heated for two minutes. It is then acidified by 25% sulphuric acid, and potassium iodide and starch are added. By the amount of iodine liberated by excess of the copper in acid solution, which is titrated by thiosulphate solution, the amount of copper reduction which has taken place can be determined. S. B. S.

**Titration of Diabetic Sugar.** IVAR BANG (*Pharm. Zeit.*, 1911, 56, 436).—The author's method (titration with copper hydrogen carbonate and hydroxylamine, *Abstr.*, 1907, ii, 136) may be safely applied to urines, and is recommended for that purpose by Hammarsten and other writers. The reason that some analysts have failed to get correct results with urines is probably due to the fact that their samples were not sufficiently diluted, as the process becomes untrustworthy when 10 c.c. of urine contain more than 0.06 gram of dextrose. L. DE K.

**Estimation of Sugar and of Calcium in the Residues from Sugar Purification.** LÉON LINDET (*Bull. Assoc. chim. Sucr. Dist.*, 1911, 28, 776—778).—A preliminary communication in which the author suggests that phenol should be added to decompose the calcium succrate, the sugar then being determined by means of the polarimeter. E. J. R.

The Detection of Sucrose in Wine by Rothenfusser's Process. F. SCHAFFER and E. PHILIPPE (*Chem. Zentr.*, 1911, i, 1256; from *Mitt. Lebensmittelunters. Hyg.* 1, 303—311).—Rothenfusser's test for added sucrose in wines (blue coloration with diphenylamine, *Abstr.*, 1910, ii, 463) is not characteristic for sucrose, but is also given by other saccharine matters, and cannot, therefore, be employed.

L. DE K.

Detection of Sucrose in Wine, White Beer, etc. S. ROTHENFUSSER (*Zeitsch. Nahr. Genussm.*, 1911, 21, 554—555).—A provisional reply to Schaffer and Philippe (see preceding abstract). The author states, however, that minimal quantities of levulose interfere with the diphenylamine test for sucrose.

L. DE K.

Valuation of Turpentine Oils. PETER KLASON (*Chem. Zeit.*, 1911, 35, 537—539).—The value of turpentine oil in practice depends on the rapidity with which it absorbs oxygen, and the author has devised a method of determining the relative values of turpentine oils from this point of view, depending on the oxidation of cymyl mercaptan by the peroxide formed in the turpentine oil.

Fifty c.c. of the oil are distilled in a current of carbon dioxide, and 10 c.c. of the distillate are set aside in an open beaker in diffused light during twenty-four hours. Five c.c. of this oxidised oil are placed in a 30 c.c. flask with a like quantity of cymyl hydrosulphide solution (5% by volume) in alcohol. This quantity of cymyl mercaptan requires 13.3 c.c. of  $N/10$ -iodine solution when titrated by Klason and Carlson's method (*Abstr.*, 1906, ii, 255). The flask is filled completely with alcohol, corked, and set aside during twenty-four hours. At the end of this time the contents are titrated with  $N/10$ -iodine solution, more alcohol being added if necessary to maintain complete solution. The difference between the number of c.c. of  $N/10$ -iodine used and 13.5 is proportional to the oxygen-absorbing capacity of the oil. For French turpentine oil, it is about 5 c.c., for "pine wood oil" about 3 c.c., and for "resin spirit," 1.5 c.c.

T. A. H.

Analysis of Camphor. WILHELM LENZ (*Arch. Pharm.*, 1911, 249, 286—298).—In connexion with an examination of camphor oil and crude camphor produced in German East Africa, the author has investigated methods for the assay of camphor, and finds that the melting point, quantity of non-volatile residue, yield of oxime, and solubility in hydrochloric acid are useful criteria in gauging the purity of samples.

The camphor oil when kept during fourteen days at 0° deposited 4.4% of camphor. The moisture in the crude camphor was determined by dissolving a known weight of the camphor in light petroleum, separating the water in a centrifugal machine, and measuring its volume. Pure camphor melted at 178.75°. Synthetic camphor had  $[\alpha]_D + 1.76^\circ$  in benzene, and this low rotation served to distinguish it from natural *d*-camphor ( $[\alpha]_D = +41.87^\circ$  in benzene under the same



conditions). The impurities in the crude camphor examined caused it to have a slightly higher dextrorotation,  $[\alpha]_D = +42.17^\circ$ , than pure *d*-camphor. The non-volatile residue was determined by heating 5 grams of the camphor on the water-bath until the residue was odourless. The time required varied from eleven to sixteen hours, and the residue left varied from 0.02% in the case of good commercial Japanese camphor to 0.298% for the East African product. The yield of oxime obtained varied from 89% for synthetic camphor to 93% for good commercial camphor. Bohrisch's test (*Pharm. Zentr.-h.*, 1907, 28, 527, 777) gave with the natural camphors reddish colorations changing to bluish-violet or bluish-green, whilst with synthetic camphor it gave a yellow coloration with a trace of vermilion-red. Good commercial camphor was completely soluble in concentrated hydrochloric acid, but synthetic camphor and the crude African camphor left noticeable quantities of undissolved matter with this solvent (compare Istrati and Zaharia, *Abstr.*, 1899, i, 225).

T. A. H.

**Estimation of Free Acid in Fats.** EYVIND BÖDTKER (*Chem. Zeit.*, 1911, 35, 548).—Five to 15 grams of fat are melted if necessary, and shaken in a stoppered bottle with 25 c.c. of alcohol, 50 c.c. of water, 2 or 3 drops of phenolphthalein are added, and the mixture titrated with *N*/10-sodium hydroxide to a deep red coloration. After shaking, the excess of alkali is titrated back with *N*/10-hydrochloric acid. The suggestion of Loebell to titrate in an alcoholic benzene solution of the fat is criticised as impossible.

E. F. A.

**Estimation of Volatile Fatty Acids in Fæces.** ROBERT S. MCCAUGHEY (*Zeitsch. physiol. Chem.*, 1911, 72, 140—150).—A method is described, the principle of which is to obtain an alcoholic extract of the fæces, and this is distilled in a vacuum with steam after the addition of phosphoric acid. The distillate is titrated with decinormal sodium hydroxide. Previous results obtained by other methods are not trustworthy.

W. D. H.

**Estimation of Tartaric Acid in Tartrates and Wines by Precipitation as Calcium Racemate.** ANDRÉ KLING (*Bull. Assoc. chim. Sucr. Dist.*, 1911, 28, 893—903).—The process is briefly as follows: To the solution of the tartrate (which in natural products is always dextrorotatory) is added a sufficiency of levorotatory alkali tartrate, thus forming a racemate which is then precipitated by addition of acid calcium acetate. The precipitate is washed with cold water and dissolved in boiling 4% hydrochloric acid, from which it is then reprecipitated by boiling with an excess of acid sodium and calcium acetate; any levorotatory calcium tartrate contained in the racemate is thus got rid of.

When cold, the precipitate is washed and dissolved in boiling dilute sulphuric acid, and, while boiling, titrated with standard potassium permanganate which has been checked against tartaric acid. The result is, of course, divided by two.

L. DE K.

**Rapid Method of Estimating Uric Acid in Urine.** P. P. PIZZORNO (*Boll. Chim. Farm.*, 1911, 50, 237—238).—A quantity of  $N/20$ -iodine solution is added to the urine (previously boiled and decolorised with animal charcoal), and the excess of iodine is estimated with thiosulphate. The difference represents the amount used in oxidising the uric acid to alloxan and urea. If the urine contains solid uric acid, this is brought into solution by adding sodium carbonate. Albumin is removed by acidifying the urine with acetic acid, adding sodium chloride, and boiling for half an hour.

R. V. S.

**Assay of Bismuth Salicylate.** HUBERT CARON and D. RAQUET (*Ann. Chim. anal.*, 1911, 16, 177—179).—The author proposes the following process for the detection and colorimetric estimation of bismuth oxynitrate in commercial bismuth salicylate: 0.5 gram of the sample is boiled for ten minutes with 50 c.c. of  $N/10$ -sodium hydroxide, and after diluting to 100 c.c. the solution is filtered and 3, 10, or even 50 c.c. (according to the nitrate supposed to be present) are evaporated to dryness. The residue is well mixed with 1 c.c. of pure sulphuric acid and 10 c.c. of water, and then 10 c.c. of ammonia are added. Owing to the action of the nitric acid on the salicylic acid which is also present, a nitro-derivative is formed which dissolves in ammonia with a yellow colour. The colour is then matched with that obtained from a mixture containing a known weight of sodium nitrate.

L. DE K.

**Schardinger's Milk Reaction.** W. RULLMANN (*Biochem. Zeitsch.*, 1911, 32, 446—472).—Germ-free, and germ-containing unheated milk, with thermostable substances, both in combination and alone, decolorise Schardinger's methylene-blue-formaldehyde reagent in a few minutes at 45—50°. The aldehyde can be substituted by formic acid in equivalent quantity, but the reaction takes longer. The decolorisation in heated milk is due to thermostable substances alone. The age of the germ-free milk exercises no influence on the reaction. If sodium hydroxide, ammonia, or phosphate is added to sterilised milk, the reaction is hastened, especially if lactose is added simultaneously; the latter alone exerts no action. Raw, pasteurised, and sterilised milk behave differently with regard to the decolorisation. This difference may be partly due to a change in the inorganic constituents produced by heat, as well as to the injury to the enzymes. The author discusses the value of the Schardinger and other reactions for discriminating between raw and heated milk.

S. B. S.

**Colour Reactions of Aromatic Aldehydes and their Application in the Analysis of Spirits.** THEODOR VON ELLENBERG (*Chem. Zentr.*, 1911, i, 1254—1255; from *Mitt. Lebensmittelvers. Hyg.* 1, 311—350. Compare *Abstr.*, 1910, ii, 805).—In addition to the higher alcohols, the terpenes which occur particularly in rum, but less in cognac, also give the reaction with salicylaldehyde and sulphuric acid. Aldehydes and acetals also give the test; the

destruction of these three series is carried out by boiling with *N*/10. silver nitrate and *N*/10-potassium hydroxide; acetals should be first hydrolysed with sulphuric acid. The results of the investigation show that Komarowsky's colour reactions occur with all unsaturated substances, and also with those that are converted into unsaturated compounds by heating with sulphuric acid; unsaturated substances in which the  $\text{CO}_2\text{H}$ -group compound is adjacent to the double bond form an exception. The reaction also occurs with aldehydes and phenols in which the para-position is not substituted. Phenols then form colouring matters of the rosolic acid type, whilst alcohols give the reaction because they are converted into olefines, which then react. The reaction is given by all the aromatic aldehydes; salicylaldehyde is preferable to the others, as it, apparently, does not react with methyl and ethyl alcohols. By treatment with sodium hydroxide, the acetals, aldehydes, and terpenes are not always completely got rid of, but addition of silver nitrate causes their complete removal.

L. DE K.

**Detection of Traces of Hydrogen Cyanide.** G. DRUCE LANDER and A. E. WALDEN (*Analyst*, 1911, 36, 266—270).—The authors have found that extremely dilute solutions of hydrogen cyanide (0.00002 gram, or less, per c.c.) may, after addition of alkali, be boiled down without suffering decomposition, and recommend the following test: To the solution (or distillate) are added 2 drops of 10% sodium hydroxide solution, and the liquid is evaporated, finally in a test-tube, nearly to dryness. One drop of 2% ferrous sulphate solution is added, and after ten or fifteen minutes 2 to 3 drops of hydrochloric acid, when the whole is warmed gently and then cooled. A blue or bluish-green colour shows the presence of hydrogen cyanide. The process is quite equal in delicacy to (perhaps superior to) the picrate test.

L. DE K.

**Estimations with Mercuric Nitrate.** LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1911, 249, 253—259).—The method suggested by Cohn (*Abstr.*, 1902, ii, 50) and applied by Rupp and Krauss (*ibid.*, 475) has been tried as a general method for the estimation of cyanides and haloid salts, by adding excess of standard mercuric nitrate and titrating back with ammonium thiocyanate, in presence of iron alum and nitric acid. Good results were obtained with hydrocyanic acid, alone or in presence of benzaldehyde cyanohydrin, cyanides, bromides, and iodides, including ferrous iodide in the pharmacopœial "syrup," but not with chlorides.

T. A. H.

**Assay of Calcium Cyanamide ("Kalk Stickstoff").** R. MONNIER (*Chem. Zeit.*, 1911, 35, 601—602).—*Estimation of Nitrogen Present as Cyanamide.*—One gram of the sample is mixed with 100 c.c. of water and stirred for two and a-half hours; 25 c.c. of the solution are evaporated in a dish, with addition of 10 c.c. of formic acid, to near dryness; the residue is made up with water to 25 c.c., 10 c.c. of this are introduced into the ureometer, and the nitrogen evolved by hypobromite from the urea generated is measured. A check experi-

ment is then made with 10 c.c. of a urea solution containing about the same weight of urea as that found in the solution of the sample.

*Estimation of the Total Nitrogen.*—Concordant results are obtained by conversion into ammonia by heating 0.5 gram of the substance with 30 c.c. of pure sulphuric acid and 1 gram of anhydrous copper sulphate; addition of potassium sulphate, phosphoric oxide, or metallic mercury offers no advantage in this case. When, however, treated according to the process used for nitrates (heating with sulphuric acid with addition of salicylic acid and sodium thiosulphate, or zinc dust), decidedly higher results are obtained.

It is therefore certain that "Kalk Stickstoff" contains its nitrogen in at least three different forms. A specimen analysed by the author showed 21.5% of total nitrogen by the salicylic acid method, and 20.5% by the copper sulphate method; 18.98% were present as cyanamide.

L. DE K.

*Improvement of the Micro-sublimation Process and the Detection of Arbutin in Plants.* O. TUNMANN (*Ber. Deut. pharm. Ges.*, 1911, 21, 312—319).—Glucosides such as arbutin cannot be sublimed, and consequently cannot be detected in plants by heating a small portion of the ground plant and applying ordinary microchemical methods to the sublimate. Arbutin is, however, readily hydrolysed by emulsin or by dilute hydrochloric or sulphuric acid, and the mixture when heated carefully on an object-glass gives a sublimate of quinol, which may be identified by its crystalline form and reactions, such as that with ammonia. The presence of arbutin in bearberry leaves and other plants can be demonstrated in this way by moistening the ground material with dilute hydrochloric acid, and after a few minutes heating it on an object-glass and collecting the sublimate of quinol on a second object-glass.

T. A. H.

*Estimation of Cantharidin in Cantharides and its Tincture.* HERMANN EMDE (*Arch. Pharm.*, 1911, 249, 259—285).—This paper gives a critical résumé of work done independently by A. KNEIP, N. NEY, and F. REIMERS in a competition for the Hagen-Bucholz prizes of the Deutscher Apotheker-Verein in 1909-10. It gives a résumé of the chief methods so far devised for the estimation of the "total," "free," and "combined" cantharidin in cantharides, including those of Léger (*Abstr.*, 1903, ii, 517), Singh (*Abstr.*, 1907, ii, 994), Walbum (*Abstr.*, 1909, ii, 839), and Greenish and Self (*Pharm. J.*, 1907, p. 324), with results obtained by the three workers named by the use of these various methods. As a result of his work Kneip suggests a new method in which the cantharides, acidified with hydrogen chloride in alcohol, is extracted with a mixture of light petroleum and benzene in a Soxhlet apparatus, and the extract so obtained freed from fat and other impurities by washing with a mixture of alcohol and light petroleum. This gives the "total cantharidin," the quantity "free" being estimated in like manner without acidifying the crude drug. Ney suggests a modified form of the Panchaud-Siegfried process, and Reimers a combination of the method devised by Fromme with that of the fifth German Pharmacopoeia.

In an appendix to the paper the results of determinations by Kneip and by Reimers of moisture, fat, and ash in commercial cantharides are given.

T. A. H.

**A Reaction for Caulophyllin.** JOHN F. H. GILBARD (*Analyst*, 1911, 36, 270—271).—Five c.c. of an alcoholic extract obtained by digesting 0.1 gram of caulophyllin in 25 c.c. of 80% alcohol are filtered and evaporated on the water-bath in a flat porcelain capsule. The residue is taken up with 1 c.c. of water, and broken up with a flat-headed rod. Two c.c. of strong sulphuric acid are then added slowly and the mixture well stirred. An intense purple-blue colour is produced within five minutes; sometimes the colour is more of a reddish-purple. When testing a mixture of drugs, for instance, a compound pill, 0.1 gram of the pill is thoroughly extracted with 80% alcohol, the filtrate is evaporated, and the residue tested as directed. The extracts of many other drugs do not give the reaction.

L. DE K.

**Estimation of Urea in Urine.** VALDEMAR HENRIQUES and S. A. GAMMELTOFT (*Chem. Zentr.*, 1911, i, 1450; from *Skand. Arch. Physiol.*, 1911, 25, 153—168).—The process given by Levene and Meyer (defecation with phosphotungstic acid, and conversion of urea into ammonia by heating with sulphuric acid in an autoclave: *Abstr.*, 1909, ii, 709) is recommended.

L. DE K.

**Identification of Veronal.** ARMAND JORISSEN (*J. Pharm. Chim.*, 1911, [vii], 3, 478—481).—The author suggests an extension of the test described in the Swiss Pharmacopœia for the identification of "veronal" (diethylbarbituric acid).

Three grams of potassium hydroxide are melted in a nickel capsule, and to this 3 grams of "veronal" are gradually added and the heating continued during ten minutes. The cold "melt" is dissolved in water (10 c.c.). This liquid gives (1) the Prussian blue reaction for cyanides, (2) carbon dioxide on addition of an acid, and the acidified solution on extraction with ether yields, after evaporation of the ether, oily drops having an odour of rancid butter and giving a wine-red coloration with ferric chloride. When "veronal" is mixed with quicklime and the mixture is gently heated on platinum foil, inflammable vapours are evolved, and the residue acquires a cinnabar-red coloration.

T. A. H.

**Identification of Cocaine and Some Cocaine Substitutes** FRANCIS J. SMYTER and FREDERIC ENGER (*Amer. J. Pharm.*, 1911, 83, 195—201).—The tests are based on the fact that a 2% solution of cocaine hydrochloride yields characteristic crystals on adding a 1% solution of either gold chloride, platinum chloride, or potassium permanganate; a 5% solution of chromic acid is also a valuable microchemical reagent. For the exact form of the crystals of the gold, platinum, and permanganate cocaine compounds, the micrographs in the original article should be examined, and for further details the tabular review of the microscopic tests should be consulted. A good chemical reagent for distinguishing cocaine and its substitutes is found

in chlorine water. To 1 c.c. of a 1% solution of the alkaloid are added 2 c.c. of strong chlorine water. Cocaine gives no precipitate;  $\alpha$ -eucaine, a milky turbidity;  $\beta$ -eucaine, a dense white turbidity; stovaine, a light milky turbidity; holocaine, a light yellow turbidity; acocaine, a maroon precipitate and claret solution, but euphtalmine gives no reaction.

L. DE K.

**The Permanganate Test for Cocaine.** FRANCIS J. SEITER (*Amer. J. Pharm.*, 1911, 83, 265—268).—The author has improved this test and now operates as follows: To one c.c. of cocaine hydrochloride solution is added one drop of 25% sulphuric acid and 1 c.c. of saturated potassium permanganate solution. After some time, a drop of the liquid is removed to a slide, the cover glass is adjusted, the excess of liquid removed, and a drop of water drawn under the cover glass by means of a piece of filter paper placed on the opposite side. The slide is then examined under the microscope for the characteristic violet-red, rectangular plates of cocaine permanganate. One part of cocaine may thus be detected when dissolved in 3000 parts of water.

Accompanying natural alkaloids and also cocaine substitutes are at once oxidised with the exception of  $\alpha$ -eucaine and  $\beta$ -eucaine. The  $\alpha$ -compound yields violet-red crystals resembling ammonium magnesium phosphate in highly diluted solutions (limit 1 : 5000), but leafy crystals in 1% solutions, whereas the  $\beta$ -compound gives, in 1% solutions, minute violet-red globules which do not crystallise when kept.

L. DE K.

**Direct Estimation of Creatine in Pathological Urine.** G. STANLEY WALPOLE (*J. Physiol.*, 1911, 42, 301—308).—The pink colour given in alkaline solution by creatine and not by creatinine when a trace of diacetyl (dimethyl diketone) is added can be utilised for the colorimetric estimation of creatine in urine. The method is simple, rapid, and fairly accurate in cases where the Folin method was used as a control.

W. D. H.

**Polarimetric Estimation of Nicotine in Tobacco Extract.** JOSEF VON DEGRAZIA (*Chem. Zentr.*, 1911, i, 1085; from *Fach. Mitt. österr. Tabakregie*, 1910, 87—90).—Thirty grams of the sample are mixed with 3.5 grams of calcium oxide and 10 c.c. of water, and the nicotine liberated is rapidly distilled in a current of steam. When the weight of the distillate is six times that of the amount of extract used, the nicotine is practically all recovered. After observing the rotation of the distillate in a 20 cm. tube in a Lippich half-shadow polarimeter, the percentage of nicotine is found from the equation  $P = a.G.f/g$ , in which  $G$  = weight of distillate,  $g$  = weight of the extract taken, and  $f$  = the rotation constant; this varies with the temperature, and a table in the original paper should be consulted.

L. DE K.

**Estimation of Nicotine in Tobacco.** JOSEF VON DEGRAZIA (*Chem. Zentr.*, 1911, i, 1085—1086; from *Fach. Mitt. österr. Tabakregie*, 1910, 149—152).—Twenty grams of finely powdered

tobacco are treated in a 300 c.c. flask with 7 c.c. of potassium hydroxide solution (1:1), a few grams of sodium chloride, and 150 c.c. of boiling concentrated brine. After distilling off rapidly, 45 c.c. of the remainder of the nicotine is distilled in a current of steam until the distillate measures 100 c.c. In the case of samples very rich in nicotine, a little more distillate should be collected. After introducing the steam, the heating of the flask should be interrupted for a while so as to dilute the residue somewhat. The distillate is then weighed and polarised (see preceding abstract).

L. DE K.

**Estimation of Nicotine in Tobacco and in Green Plants of "Nicotiana Tabacum."** R. MELLET (*Chem. Zentr.*, 1911, i, 1561; from *Schweiz. Woch. Chem. Pharm.*, 1911, 49, 117—120).—The finely cut up material (30 grams of dry tobacco or 250 grams of the green plant) is treated with boiling water in an air-tight flask, and then allowed to cool. After twenty-four hours, milk of lime is added, the stopper is again inserted, and the contents frequently shaken for another twenty-four hours. The liberated nicotine is then distilled in a current of steam until the volume of the distillate is about three times that of the original liquid. The distillate is acidified with sulphuric acid, strongly concentrated out of contact with the air, and then shaken with ether after adding potassium hydroxide. The ethereal solution is evaporated until the vapours no longer contain ammonia, and then allowed to evaporate spontaneously. The residue is then dissolved in water and titrated with *N*/10-sulphuric acid.

A number of check experiments made by the author have shown that 0.06 gram of nicotine should be added to the amount found.

L. DE K.

**Estimation of Nicotine in Tobacco Extracts.** WILHELM KOENIG (*Chem. Zeit.*, 1911, 35, 521—522).—Twenty grams of the sample are mixed in a spacious glazed porcelain dish with ignited silver sand and 4 c.c. of aqueous sodium hydroxide (1:1), and to the half-dry mass is added so much burnt gypsum that an almost dry powder is obtained. This is rubbed in a mortar and transferred to a 250 c.c. stoppered bottle. On to this powder is then delivered, from a pipette, 100 c.c. of toluene, and the mixture is frequently shaken during two or three hours. Thirty or 40 c.c. are then poured off and filtered, the funnel being kept covered, and the filtrate is now examined in the 20 cm. polarimeter tube. The rotation divided by 3.36 = nicotine in the 100 c.c. of toluene solution. As the volume of the toluene is, of course, augmented by the nicotine present, a slight correction should be applied as follows:  $x = g. 100 + g/100$ ;  $g$  = grams of nicotine in 100 c.c. of toluene solution;  $x \times 5$  = % nicotine in sample.

For the volumetric estimation, 25 c.c. of the toluene solution are placed in a stoppered flask containing 25—50 c.c. of *N*/10-hydrochloric acid diluted with 50—75 c.c. of water. After adding 25 c.c. of ether and 4 drops of iodoeosin (1 part in 500 parts of alcohol) and thorough shaking, the excess of acid is titrated, with constant shaking, with

*N*/10-sodium hydroxide; 1 c.c. of acid = 0.0162 gram of nicotine; the above correction for volume is then applied.

If the polarisation test alone is wanted, 10 grams of the extract may be diluted, if necessary, with, say, 5 c.c. of water, and, after adding 2 c.c. of alkali and some 50 glass beads, the nicotine may be extracted by shaking for two to three hours with 50 c.c. of toluene.

L. DE K.

**Theory and Modification of the Malaquin Test for Strychnine.** GEORGES DENIGES (*Bull. Soc. chim.*, 1911, [iv], 9, 537—542).—Malaquin's colour reaction for strychnine (*Abstr.*, 1910, ii, 165) is shown to depend on the action of a trace of nitric acid on a mixture of tetrahydrostrychnine and strychnidine, produced by the action of zinc and sulphuric acid on strychnine. Other oxidising agents may be used in place of nitric acid, and the author outlines a scheme for the detection of strychnine, which involves the reduction of the alkaloid with zinc and hydrochloric acid and the application of (1) sodium nitrite and (2) bromide to different aliquot portions of the reduced liquid, the former giving a rose-red, and the latter a reddish-purple coloration. The method of applying this improved Malaquin test is described in detail in the original.

T. A. H.

**Estimation of Theobromine and Caffeine.** C. MONTHULÉ (*Ann. Chim. anal.*, 1911, 16, 137—138).—0.2 Gram of the mixed alkaloids is dissolved in a small quantity of ammonia and introduced into a 100 c.c. flask, when 20 c.c. of *N*/10-silver nitrate are added. Should a precipitate form, this is redissolved by further addition of ammonia. After filling the flask up to the middle with water, a drop of phenolphthalein solution is added, and the ammonia is carefully neutralised with acetic acid. After diluting up to the mark and filtering, 30 c.c. of the liquid are titrated for silver by the Charpentier-Volhard process.

If *n* represents the number of c.c. of *N*/10-thiocyanate employed, the amount of theobromine in 100 grams of the mixture would be  $(10 - n) \times 16.6$  (according to Kunze and Génin).

The caffeine may be recovered by taking a further portion of the above prepared neutralised solution, evaporating to dryness on the water-bath with addition of sodium chloride, and extracting with chloroform.

L. DE K.

**New Applications of Amalgamated Aluminium in Analyses.** E. KORN-ABREST (*Bull. Assoc. chim. Suér. Dist.*, 1911, 28, 938—943). Amalgamated aluminium, prepared by placing aluminium turnings for three minutes in a 0.5% solution of mercuric chloride, is recommended for the defecation of solutions containing much tannin and colouring matters. The effect is due to the formation of alumina with evolution of hydrogen.

L. DE K.

**Lecithins ex ovo, A Characteristic Colour Reaction for them and a Change which they Always Undergo.** CARLO CASANOVA (*Boll. Chim. Farm.*, 1911, 50, 309—313).—The emulsion of lecithins is freed from alcohol, and extracted with ether. The concentrated



ethereal solution is treated with 2 c.c. of ammonium molybdate, then gradually with concentrated sulphuric acid. At the surface of contact of the two liquids, a cherry-red coloration appears, which becomes green and finally intensely blue. Cholesterol and phytosterol do not give this reaction. The lecithins alter readily in air, especially in aqueous suspension, and the change is accompanied by an increase in the quantity of free acid present. Alcoholic solutions are more stable.

R. V. S.

**The Use of Triketohydrindene Hydrate for the Detection of Proteins and their Cleavage Products.** EMIL ARDENHAIDEN and HUBERT SCHMIDT (*Zeitsch. physiol. Chem.*, 1911, 72, 37—43).—The blue colour given by this reagent with proteins (Ruhemann, *Trans.*, 1910, 97, 2025) is also given by peptones, and a large number of amino-acids which are enumerated. Proline, oxyproline, and pyrrolidone-2-carboxylic acid do not give the reaction; they contain an imino- instead of an amino-group. The reaction is only given by those substances which contain a free amino- and a free carboxyl group.

W. D. H.

**Protein Estimation, and Peptic Digestion of Protein.** F. WESTHAUSER (*Zeitsch. physiol. Chem.*, 1911, 72, 363—373).—The Stutzer-Burnstein method, and precipitation with tannin lead usually to the same result in protein estimations, and in the separation of protein and amide (asparagine) nitrogen. The results, however, are different if the products of hydrolysis liberated by pepsin are investigated. The applicability of such methods for the analysis of faeces is also described.

W. D. H.

**Estimation of Gliadin.** J. E. GREAVES (*J. Biol. Chem.*, 1911, 9, 271—293).—The concentration of alcohol-soluble proteins is decreased by filtering through or shaking with animal charcoal. Carefully made asbestos filters do not produce this effect; 100 c.c. of alcohol extracts 0.05% more gliadin from 8 grams of flour than it does from twice the amount of flour, but the extraction is not complete. The strength of the alcohol is a factor of importance; 74% is the best, and this extracts more gliadin when hot. Some flours contain sufficient nitrogenous substances soluble in ether to affect the accuracy of gliadin estimations. The Kjeldahl method is more accurate, although less rapid, than the polarimeter.

W. D. H.

**Hippuric Acid as the Cause of the Failure of the Spectroscopic Test for Hæmoglobin in Urine.** F. ALEX. McDERMOTT (*J. Amer. Chem. Soc.*, 1911, 33, 992—995).—The presence of hæmoglobin in urine cannot be detected by means of the absorption spectrum unless the urine is quite fresh. It has been found that if blood is introduced into normal urine, the characteristic hæmoglobin spectrum is visible at first, but the absorption bands gradually fade and ultimately disappear. It is therefore evident that normal urine contains some substance which destroys hæmoglobin.

A study of the question has shown that uric acid and carbamide do not produce any effect on the absorption spectrum of water containing a little blood, but that hippuric acid causes the bands to disappear entirely in a few minutes. If the hippuric acid is neutralised with ammonia, it no longer has the power of destroying the hæmoglobin, and the absorption spectrum remains unaffected. These results indicate that when a specimen of urine, suspected of containing hæmoglobin, has to be left for some time before the application of the spectroscopic test, it should first be rendered slightly alkaline with ammonia.

E. G.

**Detection of Blood by means of Leucomalachite Green.** FRANZ MICHEL (*Chem. Zeit.*, 1911, 35, 389—390).—The reagent is prepared by dissolving 1 gram of leucomalachite green in 85 c.c. of glacial acetic acid, and diluting the solution with water to a volume of 250 c.c. One drop of the solution to be tested for blood is treated with 5 drops of the reagent, and 2 drops of a 1% hydrogen peroxide solution. Should blood be present, a green coloration develops within a short time. As it is not always possible to prepare a completely colourless solution of the reagent, a control test, using only the reagent and hydrogen peroxide, should be made. The test will detect the presence of 0.001 mg. of blood. Iron rust, saliva, bile, and proteins do not give a coloration with the reagent, but pus sometimes gives a slight reaction.

W. P. S.

**The Estimation of Diastase in Organs.** H. SCHIROKAUER and G. G. WILENKO (*Biochem. Zeitsch.*, 1911, 33, 275—281).—Wohlgemuth's method was employed, into which two modifications were introduced, namely, the diastase was extracted from the well ground organs by agitating with saline for one hour in a shaking machine, and by shaking the digestion mixtures three times during the course of incubation (twenty-four hours) to avoid error due to sediment formation. Muscular tissue contained the largest amount of diastase, kidneys less, and liver the least of the organs investigated.

S. B. S.

**Estimation of Catalase.** O. LAXA (*Zeitsch. Nahr. Genussm.*, 1911, 21, 417—420).—An apparatus is described for estimating catalase in milk; it consists of a graduated glass tube of 20 c.c. capacity, the lower end being drawn out to form a narrow jet, whilst the upper end is fitted with a tap. A mixture of the milk to be tested and hydrogen peroxide, in the proportion of 15 c.c. of the former to 5 c.c. of the latter, is filled into the apparatus, and the volume of oxygen liberated by the action of the catalase on the hydrogen peroxide in a given period of time is ascertained; this volume is a measure of the catalytic activity of the milk. It is claimed that the apparatus yields concordant and trustworthy results.

W. P. S.

**Colorimetric Detection of Some Oxidising Substances of the Body.** W. LOELE (*Chem. Zentr.*, 1911, i, 38; from *Munch. med. Woch.*, 57, 2414—2416).—Certain cell granules have the property of forming coloured compounds with alkaline solution of phenol, which

reaction can only take place in the presence of oxidising substances. Of the  $\alpha$ -granules and the similarly behaving granules of the  $\alpha$ -leucocytes, of the epithelia of the salivary glands, etc., it may be said that the granules contain an amino-base and an oxidising enzyme (Schultzer's oxydase).

On exposure to the air,  $\alpha$ -naphthol-formol solution turns first green, then blue, and finally greyish-black. The colouring matter turns red with acids, and dissolves in chloroform. When blood-serum is added, the coloration is retarded; a 10% solution of peptone, or of Liebig's meat extract, or addition of bile has the same effect. The green colouring matter obtained behaves like a lacmoid. Boiled meat extract, however, is inactive, showing that, in this case, an oxidising enzyme is present.

L. DE K.

The Reactions of Van Deen and Adler. CORRAO BONIOVANNI (*Boll. Chim. Farm.*, 1911, 50, 201—203).—Tarugi, finding that the blue coloration with hydrogen peroxide and guaiacum or benzidine was given also by thiocyanates, has advanced the view that these reactions of blood are due to thiocyanates, which act as peroxydases, yielding peroxygenated substances which oxidise the guaiacum or benzidine. The author shows that this is improbable, because the coloration is given by chromates, small quantities of bromine and other oxidisers, so that it cannot need the presence of peroxygenated compounds. Moreover, the red solutions obtained from thiocyanates and ferric salts, which may contain a peracid, do not give the benzidine reaction.

R. V. S.

Titration of "Salvarsan" with Iodine Solutions. G. OTTO GAEBEL (*Arch. Pharm.*, 1911, 249, 241—247).—It was shown previously (this vol. ii, 448) that ordinary methods for the estimation of arsenic could not be used for "salvarsan" (diaminodihydroxyarsenobenzene hydrochloride). In the present paper the interaction of iodine with this drug is considered, and it is shown that it may be estimated by titration with iodine provided an empirical factor is used in calculating the results.

The interaction of "salvarsan" with iodine takes place in accordance with the equation  $\text{As}[\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}_2\cdot\text{HCl}]_2 \cdot 2\text{H}_2\text{O} + 4\text{I}_2 + 4\text{H}_2\text{O} = 2[\text{AsO}(\text{OH})_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}_2\cdot\text{HCl}] + 8\text{HI}$ , but in practice only  $\frac{7}{8}$  atoms of iodine are used per mol. of "salvarsan" in place of 8 as required in this reaction. This is probably due to the reversibility of the reaction. The following method of carrying out the estimation is suggested, and under these conditions 1 c.c. of  $N/10$ -iodine is equivalent to 0.006326 gram of "salvarsan." A quantity of an 0.2 to 0.5% solution of the drug, equal to 0.1 gram, is mixed with 1 c.c. of starch solution and titrated with  $N/10$ -iodine solution until a permanent blue coloration is produced.

T. A. H.

## General and Physical Chemistry.

**Optical Properties of Some Unsaturated Ketones.** FREDERICK H. GETMAN (*Amer. Chem. J.*, 1911, 45, 539—547).—In an earlier paper (Abstr., 1910, ii, 832) the surface tensions and densities of mesityl oxide, styryl methyl ketone, styryl ethyl ketone, and benzylidenepinacolin were recorded, and it was shown that these substances are non-associated. The refractive indices, dispersions, and absorption spectra have now been determined.

The refractive indices have been measured for the *D*, *C*, *F*, and *G* lines at various temperatures. In the case of styryl methyl ketone, styryl ethyl ketone, and benzylidenepinacolin (which melt at 40.2°, 75°, and 39.5° respectively), several readings were taken on the supercooled liquids; when the refractive indices are plotted against the temperatures, no discontinuity is apparent at the m. p. The molecular refractions have been calculated by the Gladstone and Dale and the Lorentz-Lorenz formulæ and compared, in each case, with the values computed from the refractivities of the elements as determined by Conrady (Abstr., 1889, 661) and Brühl (Abstr., 1891, 776). The two sets of values thus obtained agree fairly closely for mesityl oxide, but for the other compounds the observed values are much higher than the calculated; this optical exaltation is ascribed by Brühl to the relative positions of the unsaturated groups in the molecule (Trans., 1907, 91, 115; Abstr., 1908, ii, 1002). Similar large differences between the molecular dispersions and those calculated from the atomic dispersions (Brühl, Abstr., 1891, 776) are shown by all the four compounds.

The ultra-violet absorption spectra of styryl ethyl ketone and benzylidenepinacolin have been studied, and the results plotted by Baily and Desch's method (Trans., 1904, 85, 1039). The curves thus obtained have the same general form as that of styryl methyl ketone Baily and Schaefer, Trans., 1908, 93, 1813). E. G.

**The Origin of Spectra.** FRANK HORTON (*Phil. Mag.*, 1911, [vi], 21, 14—219).—The five distinct line spectra which are exhibited by mercury vapour under different conditions of electrical discharge (compare this pl., ii, 559) are attributed to the re-combination of remainder atoms of different "electric atomic weight" with the appropriate number of electrons to form neutral systems. These systems differ probably from the atoms of the unionised gas and represent less stable arrangements of positive ions with one or more electrons revolving round them, each system, however, being electrically neutral. The periods of these systems will depend on the arrangement of the electrons around the neutral positive ion. For any one system there must be several positions of equilibrium, and consequently several periods. Since a finite minimum amount of energy will be required for the production of a particular positive ion, it follows that the corresponding neutral system, and the lines to which it gives rise, will appear, when the

energy is increased up to that value. In this way the appearance of the distinct line spectra under altered electrical conditions can be accounted for. The fact that compounds always give banded spectra seems to indicate that these are due, not to electrons, but to systems of atomic dimensions vibrating within the molecule.

H. M. D.

**The Carrier and the Emission Centre of Series Lines.** JOHANNES STARK (*Jahrb. Radioaktiv. Elektronik*, 1911, 8, 231—240; *Ber. Deut. physikal. Ges.*, 1911, 13, 405—416).—A theoretical paper in which the author maintains the correctness of the hypothesis that the line spectra are due to positive ions. The actual centres of emission and absorption are supposed to be the parts of the atoms from which valency electrons have been removed.

H. M. D.

**Spectroscopic Investigations in Connexion with the Active Modification of Nitrogen. I. Spectrum of the After-Glow.** ALFRED FOWLER and (Hon.) ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1911, A, 85, 377—388).—The spectrum of the after glow of pure nitrogen is described in detail, and wave-length measurements showing the series relationships of the various bands are recorded. The bands appear to fall into three groups, the first of which contains three bright bands in the red, yellow, and green, and these have been found to be identical with some of the bands in the first positive group of nitrogen.

The second group consists of a series of eleven bands in the violet and ultra-violet extending from  $\lambda = 4312$  to  $\lambda = 2503$ ; these are degraded towards the red end of the spectrum and have double heads. Other fainter series of bands of similar structure also belong to this group.

The third group consists of a series of flutings, degraded towards the more refrangible end, which correspond in every way with Deslandres' third positive group of nitrogen bands.

The effect of introducing a condenser into the discharge circuit is to reduce the intensity of the first positive bands, to intensify the second, and to abolish those of the third positive group. At the same time a new series of seven bands makes its appearance in the ultra-violet from  $\lambda = 2904$  to  $\lambda = 2256$ . These have not been described previously, and it is suggested that they should be termed the "fourth positive" group.

When the discharge is such as to give only the line spectrum of nitrogen, there is no after-glow effect.

H. M. D.

**The Ultra-violet Bands of the Carbon Monoxide Spectrum.** PETER WOLTER (*Zeitsch. wiss. Photochem.*, 1911, 9, 361—387).—Wave-length measurements have been made of the bands in the ultra-violet spectrum emitted by Geissler tubes containing carbon monoxide. By means of Geissler tubes furnished with a Wehnelt cathode, as described by Koenen and Jungjohann (*Physikal. Zeitsch.*, 1910, 11, 112), the author has succeeded in obtaining spectra of high intensity with a continuous current discharge.

The wave-length data are examined in reference to Deslandres' bands.

and although an approximate agreement is found, the author arrives at the conclusion that these do not afford a sufficiently accurate representation of the structure of the bands.

H. M. D.

**Spectra of Combustion of Hydrocarbons and of Different Metals.** JEAN MEUNIER (*Compt. rend.*, 1911, 152, 1760—1762).—A Bunsen burner supplied with hydrogen instead of coal gas can be made to give a well-defined inner cone similar to the green one shown in the ordinary way when the air supply of a Bunsen is increased. The spectrum of this cone shows lines of calcium from floating dust. The principal lines of the spectra given by different metals burning in air are mentioned.

W. O. W.

**Circular Double Refraction of Sodium Chlorate.** GEORGES MESLIN (*Compt. rend.*, 1911, 152, 1666—1668).—Fresnel's triprism of quartz has been imitated with sodium chlorate to ascertain whether the double refraction produced in the direction of the axis in the former case would also be exhibited by an optically active substance not doubly refracting in the ordinary way. The assemblage consisted of a prism of dextrorotatory crystals having an angle of  $137^\circ$ , with two levorotatory prisms of angle  $68^\circ 30'$ . Observations with the mercury are showed that the yellow, green, and violet lines were doubled by the prism, the two components being circularly polarised in opposite directions.

W. O. W.

**Molecular Structure and Optics of Large Liquid Crystals.** OTTO LEHMANN (*Ann. Physik*, 1911, [iv], 35, 193—219).—By means of a special form of crystallisation microscope the author has examined the structure of liquid crystals of ethyl *p*-azoxybenzoate of about 1 mm. diameter. The appearances presented in ordinary and polarised light between parallel, crossed, and half-crossed nicols are illustrated and described in detail. Observations were also made with *p*-azoxyphenetole containing a little azobenzene, with *p*-azoxyanisole admixed with *p*-azoxyphenetole, resin, and oil, and with *p*-azoxyphenetole admixed with methylene iodide and resin.

H. M. D.

**Anomalous Magnetic Rotation Dispersion and Selective Absorption.** G. J. ELIAS (*Ann. Physik*, 1911, [iv], 35, 299—346).—Measurements have been made of the rotation dispersion for various substances which exhibit selective absorption, with special reference to the magnitude of the dispersion in the neighbourhood of the absorption bands.

Detailed results are recorded for aqueous solutions of praseodymium nitrate, neodymium nitrate, samarium nitrate, and erbium nitrate. Observations were also made with liquid air, water, aqueous solutions of potassium permanganate and cobalt chloride, and with uranium glass. The data are discussed in reference to the hypothesis put forward to account for the magnetic rotation of the plane of polarisation.

H. M. D.

**A Method of Optical Control for Magneto-chemical Analyses.** PAUL PASCAL (*Compt. rend.*, 1911, 152, 1852—1855. Compare this vol., ii, 91, 183, 251, 252).—From Drude's modification

of the Ketteler-Helmholtz dispersion formula (*Ann. Physik*, 1904, [iv], 14, 677) the author deduces the simplified expression:

$$N = 1841 \times 10^{-14} \cdot M r_1 r_2 (1/\lambda_1^2 - 1/\lambda_2^2) / d(r_1 - r_2),$$

in which  $M$  is the molecular weight,  $d$  the density of a substance having refractive index  $n$ ,  $\lambda_1$  and  $\lambda_2$  are the two wave-lengths for which  $n$  has been measured, whilst  $r = n^2 - 1 + k\lambda^2$ .  $N$  is found to be nearly equal to the sum of the valencies of the atoms composing the molecule, and its difference from this number,  $\Delta$ , when not zero, is shown to be closely connected with the constitutive properties of the substance.  $\Delta$  has been determined for several hydrocarbons and their halogen derivatives, and from the results conclusions have been arrived at concerning the number of electrons influencing  $n$ , which agree closely with those previously deduced from magnetic measurements.

Generally speaking, ethylenic linkings and ring-formation diminish the number of active electrons. Benzenoid hydrocarbons behave optically and magnetically as though no double linkings are present. Halogens diminish the number of electrons active in the optical sense, and, except in the case of fluorine, they also produce a diminution in diamagnetism. According to Drude's electronic theory of light the optical effect is due to mutual saturation of supplementary valencies, and the same explanation has already been adopted by the present author to account for the diamagnetic deficits in halogen compounds.

W. O. W.

**Nature of the Photochlorides of Silver and their Potential in Light.** KONRAD SICHLING (*Zeitsch. physikal. Chem.*, 1911, 71, 1—57).—The preparation of photochlorides of silver containing silver chloride and amorphous silver in varying proportions is described. From the results of solubility and of potential measurements the conclusion is drawn that the photochlorides are solid solutions of silver chloride and amorphous silver. The "half chloride,"  $\text{Ag}_2\text{Cl}$ , is doubtless present, but is not a predominant component of the system. It is probable that colloidal silver and silver chloride are miscible in all proportions. There is a definite region of stability of the photochlorides towards crystalline silver and silver chloride.

In the first experiments on the influence of light on the potential of the photochlorides, the latter were absorbed in gelatin, but later it was found more advantageous to use colloidal silicic acid as the absorbing agent. Platinum net was used as electrode, platinum chloride solution as electrolyte, and the potentials were measured against the silver/silver chloride electrode, the latter being kept in the dark. The Uviol lamp and the Nernst light were used as sources of illumination. With the former, alterations of potential up to  $\frac{1}{2}$  volt were observed, illumination rendering the electrode more positive.

The influence of the composition of the photochloride mixture, of the intensity and colour of the light, and of the temperature were investigated in detail. Photochlorides containing the components in any proportion appear to be sensitive to light. On exposure to white light, the potential gradually rises to a maximum and then diminishes somewhat. On then removing the source of light the potential gradually falls, in some cases becomes negative, and then slowly

returns to the potential before illumination. Blue and yellow have much the same effect as white light, green light has a less powerful action, and red light produces a negative potential. The maximum potential rises in an approximately logarithmic manner with the intensity of illumination. The temperature-coefficient is negative.

G. S.

[Nature of the Photochlorides of Silver and their Potential in Light.] EML BAUR (*Zeitsch. physikal. Chem.*, 1911, 77, 58—65. Compare preceding abstract).—In order to explain the complicated form of the potential curve obtained on illuminating a photochloride and then withdrawing the source of light (maximum in light, minimum in the dark, with subsequent slow return to the original potential), three processes are necessary, a positive, a negative, and an annulling. The positive process is the absorption of light energy by the silver chloride in the photochloride, whereby it becomes unstable; the annulling process is the gradual "acclimatisation" of the photochloride to light, whereby the stimulating effect of the latter diminishes. The negative action which has been observed for red light is ascribed by the author to the silver in the photochloride, also assumed to be sensitive to light, and it is shown that the results can be accounted for in this way.

The results obtained by Siebling are further shown to afford an explanation of certain phenomena observed in photography, such as solarisation.

G. S.

**Photochemical Reactions in Aqueous Solution.** ALFRED BENNATH (*Annalen*, 1911, 382, 222—235).—The action of ultra-violet (mercury) light on aqueous solutions is not so marked as its action on gases (Berthelot and Gauduchon, *Abstr.*, 1910, i, 349; ii, 564, 606, 814; this vol., ii, 240, 242; Stoklasa and Zdobnický, this vol., i, 178). The effects are similar to those of ordinary light, but more pronounced. All carboxylic acids are decomposed according to the scheme  $R \cdot CO_2H \rightarrow RH + CO_2$ . In the case of  $\beta$ -ketonic acids, this decomposition occurs in the dark when solutions of the acids are heated;  $\alpha$ -ketonic acids are decomposed when exposed to sunlight in glass vessels. Other acids are decomposed but slowly under these conditions, but decompose more readily in the presence of fluorescent salts, such as those of uranium. All acids decompose when exposed in quartz vessels to the effect of the rays from a mercury lamp. Sulphonic acids behave in a similar manner; for example, an aqueous solution of sulphanilic acid is decomposed into aniline and sulphuric acid. An aqueous solution of ether does not yield alcohol when exposed to ultra-violet light. Esters, on the other hand, are hydrolysed, whereas ester formation has not been observed. Halogen derivatives are hydrolysed; thus bromobenzene and water yield phenol and hydrobromic acid. Monochloroacetic acid yields first glycollic acid, but this is oxidised to glyoxylic acid, which is decomposed into formaldehyde and carbon dioxide. Dichloroacetic acid yields glyoxylic acid or its decomposition products, and trichloroacetic acid yields chloroform and carbon dioxide. Chloroform in aqueous suspension or aqueous alcoholic solution is



oxidised to formic acid or its decomposition products. The only manner of preventing the decomposition of chloroform is to keep it in the dark. Carbon tetrachloride and water yield carbon dioxide and hydrochloric acid. Choral hydrate is decomposed by water into carbon dioxide and formaldehyde. For hydrolytic decomposition of ketones compare Ciamician and Silber (Abstr., 1907, i, 587; 1908, i, 277, 555; 1909, i, 306, 396).

When aqueous solutions of  $\alpha$ - or  $\beta$ -hydroxy-acids are exposed to ultra-violet light in the presence of ferrous salts, ketonic acids are first formed, and these are then decomposed into carbon dioxide and aldehydes or ketones. It is not advisable to seal the tubes while they are exposed to the light, as the pressure of the carbon dioxide may be appreciable. Lactic,  $\alpha$ -phenyl-lactic, malic, and mandelic acids behave in this way. Citric acid yields acetone and carbon dioxide, acetonedicarboxylic acid probably being formed as an intermediate product. Tartaric acid is oxidised to carbon dioxide, formaldehyde, glyoxylic acid, and glyoxal.

The velocity of a photochemical reaction can be studied, in many cases, by means of the change in electrical conductivity, provided the solutions are less concentrated than normal. This is shown in the case of the reduction of ferric chloride by means of ethyl alcohol, where the value  $\Delta/t$  (increase in conductivity per minute) rises rapidly and finally becomes constant. The hydrolysis of chloroform by water is a pure photochemical reaction, and the values for  $\Delta/t$  are nearly constant, but tend to diminish as  $t$  increases. This may be due to the fact that the hydrogen chloride formed acts as a catalyst.

The hydrolysis of methyl acetate and of monochloroacetic acid has been studied in a similar manner. In the latter case a 0.6*N*. solution was used, and the values for  $\Delta/t$  increased with  $t$ , and finally attained a maximum.

Experiments have been made on the absorbing values of different liquids for the active light rays. This was effected by surrounding the narrow quartz cylinder containing the mixture under investigation within a quartz mantle and filling the space between the two vessels with the liquid. Water is the liquid most transparent to the active rays, and the benzene hydrocarbons the least. The following comparative numbers are given: Water, 100; methyl alcohol, 94; ethyl alcohol, 93; glycerol, 56; acetic acid, 31; isopropyl alcohol, 27; isobutyl alcohol, 20; isoamyl alcohol, 14; ethyl acetate, 8; methyl acetate, 5; benzene, 3; toluene, 3.

J. J. S.

**Variations in the Distribution of  $\alpha$ -Particles.** E. C. SNOW (*Phil. Mag.*, 1911, [vi], 22, 198—200).—The theory of ideal frequency curves developed by Karl Pearson has been applied to the experimental results in the paper by Rutherford and Geiger (Abstr., 1910, ii, 917) bearing the same title, to measure the "goodness of fit" of the experimental results with theory. The "fit" is described as fair for the  $\frac{3}{4}$ -minute interval and better for the  $\frac{1}{4}$ -minute interval experiments. Those authors' conclusion, that the variations of emission are not greater than is to be expected on a random distribution, is not controverted.

F. S.

**Energy Transformations of X-Rays.** WILLIAM H. BRAGG and HARRY L. PORTER (*Proc. Roy. Soc.*, 1911, A, 85, 349—365).—According to the corpuscular theory of X-rays, the passage of these through matter gives rise to cathode rays which alone cause ionisation. Since the speed of a cathode ray is determined by the hardness of the X-ray from which it is derived, it is permissible to speak of a zinc cathode ray as determining the quality of the zinc X-ray. Homogeneous tin X-rays were allowed to fall normally on plates of copper and zinc, and the energy of the zinc cathode rays and the copper cathode rays were measured in terms of the ionisation they produce. Allowing for the energy appearing as copper X-rays and zinc X-rays, it was found that the rate of production of cathode rays is proportional to the absorption of the primary tin X-rays in the metal. If plates of metals other than copper and zinc were used, or tin replaced by arsenic or zinc, this proportionality was still found to exist. This suggests that when X-rays are absorbed by matter their energy is fully accounted for by the energy of the cathode rays. If characteristic X-rays are formed, these result from the transformation of the cathode rays.

In order to show that ionisation is not directly due to X-rays, the ionisation due to cathode rays produced in silver was compared with the ionisation produced by the passage of the same beam of X-rays through oxygen. Tin X-rays were passed into a chamber closed by one, two, or more sheets of silver foil. From the curve showing the relation between cathode ray radiation and the thickness of the silver, the amount of such radiation produced in the silver could be found in terms of that emerging. When tin X-rays were passed into this chamber containing oxygen, it was found that the ionisation due to the cathode rays produced in the silver (as obtained by that emerging from the silver) was 34.3 times the ionisation produced by the X-rays in an equal weight of oxygen. Experiments also show that the absorption coefficient of tin X-rays in silver was thirty-six times greater than that in oxygen, weight for weight. According to the corpuscular theory this means that the cathode ray production in silver is thirty-six times greater than that produced in oxygen, and these results, therefore, indicate that the whole of the ionisation in oxygen must be attributed to the cathode rays. H. M. D.

**Chemical Action of Canal Rays.** VOLKMAR KOHLSCHÜTTER (*Zeitsch. Elektrochem.*, 1911, 17, 393—398).—Referring to the experiments of Dechend and Hammer (this vol., ii, 454) the author describes a number of observations of the action of canal rays on metals and salts. In general, the changes observed are independent of the nature of the gas in which the rays are produced, although they take place more readily in a gas of higher molecular weight. The author thinks that the changes are probably due either to the mechanical effects of the impact of atoms moving at a high velocity or to the heat developed by the impact; specific chemical reactions of the rapidly moving atoms have not as yet been definitely recognised.

T. E.

**The Transformation of the Actinium Emanation.** HANS ZEIGER (*Phil. Mag.*, 1911, [vi], 22, 201—204).—The occurrence of

double scintillations, using the  $\alpha$ -rays of the actinium emanation, gave rise to the presumption that the change of the emanation was either accompanied by the expulsion of two  $\alpha$ -particles, or that it was duplex, the period of the  $\alpha$ -ray product of the emanation being less than 0.1 second (Geiger and Marsden, *Abstr.*, 1910, [ii], 92). Experiments on the range of the  $\alpha$ -rays of the actinium emanation have shown that the  $\alpha$ -rays consist of two types, the ranges of which, in air, are 5.7 and 6.5 cm., the range of the  $\alpha$ -ray of the active deposit being 5.4 cm. The  $\alpha$ -ray of actinium- $X$  has a range of 4.4 cm., Hahn having ascribed to actinium- $X$  the longer-ranged  $\alpha$ -ray given by the emanation. Further evidence has been obtained that the  $\alpha$ -ray of 6.5 cm. range is due to a product of the emanation, having a period of the order of 1/500th second, that due to the emanation itself having the range of 5.7 cm. An arrangement was used whereby only the longest range  $\alpha$ -rays could reach the screen from a tube with a thin mica window in which actinium emanation circulated. Inside the tube was placed an electrode, so that no  $\alpha$ -rays proceeding from the electrode could escape from the mica window. Application of a field to the inner electrode and the tube greatly reduced the number of  $\alpha$ -rays reaching the screen, showing that the product of the emanation gives  $\alpha$ -rays and carries a charge. From the field necessary to effect a certain reduction in the number, and by assuming that the radioactive atoms possess the same migration constant as positive ions, a rough estimate of the order of the period of the product was obtained.

F. S.

**A New Radium Perpetuum Mobile.** HEINRICH GREINACHER (*Ber. Deut. physikal. Ges.*, 1911, 13, 398—404).—This apparatus is in principle the same as in that of the Curies' first demonstration of the negative charge carried by the  $\beta$ -rays of radium. A metal plate, completely embedded in paraffin wax, absorbs the  $\beta$ -rays from a radium source and becomes negatively charged. The plate is connected, by a fine wire embedded in paraffin wax within a metal tube, with the needle of a "binant electrometer" placed at a considerable distance to avoid the ionisation of the air around the needle by the radium. The "binant electrometer" is a kind of quadrant electrometer with a single pair of opposite quadrants, one carrying a platinum wire for discharging the needle when the deflection attains a certain value. The needle is charged up negatively, and discharged alternately at a definite constant rate if an external separate radium preparation is placed upon the embedded metal plate, or brought near to it, so that  $\beta$ -rays penetrate to the plate. The instrument is arranged for use with a mirror and scale for lecture demonstration, and possesses the advantage that it can be worked with any available preparation of radium.

F. S.

**A Readily Absorbable, Ionising Radiation Emitted by Radium-C.** LOUIS WERTENSTEIN (*Compt. rend.*, 1911, 152, 1657—1660. Compare *Abstr.*, 1910, ii, 817).—The radiation giving rise to strong ionisation, to which attention has previously been drawn, appears to be produced by the projection of radium- $D$  from radium- $C$ , since its

intensity is always proportional to the amount of radium-C on an active disk, and it is only slightly deviated by a magnetic field of moderate intensity.

W. O. W.

**The Estimation of Radium Emanation by the Ionisation Current.** W. S. TROFF (*Physikal. Zeitsch.*, 1911, 12, 476—480).—Details are given of a comparison of Mache's method and Elster and Geitel's apparatus with Schmidt's method and instruments in the estimation of radium emanation in the water of a thermal spring of W. Siberia. The values obtained by the former method were more constant and somewhat lower than those obtained by the latter, using the strength of the ionisation current in the electroscope as the basis of comparison. The conditions for using the ionisation current as a measure of the quantity of radium emanation are discussed, and the importance is emphasised of passing the gas from the spring-water through cotton-wool and a drying agent before admitting it to the electroscope. Under proper conditions the two methods give similar results.

F. S.

**Effect of Electric and Magnetic Fields on the Spontaneous Charging of Polonium. The Penetration Power of  $\delta$ -Rays.** F. HAUSER (*Physikal. Zeitsch.*, 1911, 12, 466—476).—In a vacuum a polonium plate charges itself positively, the  $\delta$ -rays carrying away more negative electricity than compensates for the positive charges of the  $\alpha$ -rays. The limiting potential attained, if the plate is perfectly insulated, is about 24.5 volts, whilst a potential of 3.91 volts suffices to reduce the loss of negative electricity to half-value. This was determined by measuring the rate of loss of charge when the polonium was charged both positively and negatively, with and without a magnetic field sufficient to return the  $\delta$ -rays to the plate. The limiting potential  $E$  is given by  $E = mv^2/2e$ , where  $m$ ,  $v$ , and  $e$  refer to the mass, velocity, and charge of the  $\delta$ -ray. The secondary rays produced by the impact of the  $\alpha$ -rays on brass have a value for  $mv^2/e$  certainly not greater than for the  $\delta$ -rays. From the rate of charging of the polonium plate and its surroundings with and without a magnetic field, it is deduced that per  $\alpha$ -particle expelled about 60  $\delta$ -particles are expelled, and that each  $\alpha$ -particle produces about 17 secondary negatively-charged particles by impact on brass. By measuring the rate of charging of a polonium plate covered with thin aluminium foil, it was deduced that the  $\delta$ -particles have a penetration power of from 1/7th to 1/11th of the penetration power of the  $\alpha$ -rays of polonium.

F. S.

**A Method of Investigating the Quantity of Radium in Rocks and Minerals, etc.** JOHN JOLY (*Phil. Mag.*, 1911, [vi], 22, 134—150).—The emanation is removed from the rock or mineral by fusion with sodium and potassium carbonates or with borax. This is accomplished in a platinum crucible, electrically heated by a resistance wire within a porcelain crucible, and covered with a quartz bell-jar. The crucible rests on an iron plate standing in water on feet, and the quartz bell-jar is made air-tight by dipping in mercury contained in an annular groove in the iron plate. The expelled gases are collected

in a rubber bag and discharged into the electroscope, arrangements being provided for sending a current of air through the apparatus at the close of the fusion.

The results obtained show that this method removes more emanation and indicates a higher radium-content than the solution method. Acid rocks especially, owing to the intense effervescence, yield their emanation easily, but the same result may be attained with basic rocks by addition of boric acid. The new method showed in two series of Irish granites a mean radium-content 46% higher than the solution method, whilst with basic rocks much larger increases, up to four times the earlier results, were obtained. No radium could be detected in the reagents used by the new method, and no appreciable loss of emanation could be observed from a sample of rock after being kept in a closed vessel for a month. The advantages of the fusion method are its quickness, the small bulk of the materials employed, and greater certainty against contamination of the materials tested. F. S.

**A New Radioactive Mineral Spring at Brambach i.V.** HEINRICH FRESSENIUS and A. CZAPSKI (*Chem. Zeit.*, 1911, 35, 722—723).—The radioactivity, measured at the spring, was found to be 2270 Mache units. Experiments made on water which had been kept for some days showed that the half-period was 3.02—3.13 days, which is less than that corresponding with pure radium emanation (3.71—3.86 days). Further measurements lead the authors to the conclusion that the 2270 Mache units are chiefly due to radium emanation, but that another radioactive substance is present which has a shorter life-period than radium emanation.

The waters of this spring are by far the most radioactive known. T. S. P.

**Radioactive Springs of Exceptionally High Activity at Brambach in the Saxon Vogtland.** M. WEIDIG (*Zeitsch. öffentl. Chem.*, 1911, 17, 221—224. Compare the preceding abstract).—The radioactivity of the new spring is given as 1965 Mache units. The radioactivities of the waters from six other springs at Brambach are also given; they vary from 81 to 361 Mache units. T. S. P.

**Charges on Ions in Gases.** JOHN S. TOWNSEND (*Phil. Mag.*, 1911, [vi], 22, 204—211).—The evidence in favour of the view that positive ions carrying double charges are produced in gases in certain circumstances is reviewed, the opposite conclusion (Millikan and Fletcher, this vol., ii, 573) being criticised. Various criticisms of the author's results (*loc. cit.*) are replied to. F. S.

**Corpuscular Ionisation of Saline Vapours and the Re-combination of Ions in the Flame.** GEORGES MOREAU (*Compt. rend.*, 1911, 152, 1664—1666. Compare this vol., ii, 455).—In the production of ions in a flame charged with the vapour of a salt, under the conditions previously described, the saturation current,  $I_0$ , is not experimentally attainable, but can be deduced from observations made with fields of low intensity. With intense fields, return of corpuscles

to the cathode through diffusion is comparatively insignificant, and consequently the number of salt molecules,  $p$ , dissociated by each cathodic corpuscle is given by the expression  $p = Q/Q'$ , where  $Q'$  is the observed current.

It is found that  $p$  does not vary with the acid radicle of the salt, and only within narrow limits with the metallic radicle. The value of  $p$ , however, changes with the incandescent substance coating the cathode, its temperature, and the duration of heating. At about  $1500^\circ$ ,  $p$  does not exceed 20 for lime or 10 for strontium oxide, barium oxide, or sodium carbonate. The coefficient of re-combination of ions varies between 5000 and 20,000 electrostatic units, according to the nature of the salt and material of the cathode. It follows that re-combination occurs once in about 500 collisions. W. O. W.

Experiments with Liquid Helium-D. Change of the Electrical Resistance of Pure Metals at Very Low Temperatures. V. Disappearance of the Resistance of Mercury. H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 113—115. Compare this vol., ii, 487, 575).—More accurate measurements have been made of the resistance of mercury at helium temperatures. At  $4.3^\circ$  abs. the resistance is 0.0021 of the value for solid mercury at  $273^\circ$  abs., whereas at  $3^\circ$  abs. it is only 0.0000001 of the value at  $273^\circ$ . Further lowering of the temperature to  $1.5^\circ$  abs. produces no measurable alteration in the resistance. These results indicate that the upper limit to be ascribed to the resistance, which still remains at helium temperatures, is very much smaller than the limit deduced from the earlier determinations.

H. M. D.

Dissociation of Sulphuric Acid and the Mobility of the Hydrogen Sulphate Ion. KARL DRUCKER (*Zeitsch. Elektrochem.*, 1911, 17, 398—403. Compare Abstr., 1907, ii, 610; 1910, ii, 937; and this vol., ii, 362).—It would be possible to calculate the dissociation constant  $k_2$  of the change  $\text{HSO}_4' \rightleftharpoons \text{H}' + \text{SO}_4''$  from measurements of the conductivity of sulphuric acid if the fraction of the acid dissociated according to the equation  $\text{H}_2\text{SO}_4 = \text{H}' + \text{HSO}_4'$  and the mobility of the  $\text{HSO}_4'$  ion were known. Earlier writers have attempted to calculate  $k_2$  by assuming values for these quantities; it appears, however, that the value assumed for the mobility of  $\text{HSO}_4'$  affects the result very little; the degree of the first stage dissociation is the important factor. The writer has therefore studied sodium hydrogen sulphate. New measurements of the depression of freezing point and of the concentration of hydrogen ions by means of a concentration cell show, in good agreement with each other, that a 0.1*N*-solution of sodium hydrogen sulphate contains 0.049 gram-mol. of  $\text{H}'$  ion per litre. Combining these results with the migration and conductivity measurements of Noyes and Stewart (Abstr., 1910, ii, 937), the value of the mobility of the  $\text{HSO}_4'$  ion at  $25^\circ$  is found to be 39. The values of  $k_2$  are then calculated from the conductivity of sodium hydrogen sulphate solutions on the assumptions (1) that the first stage dissociation is complete, (2) that it is equal to that of sodium chloride, and

(3) that it is equal to that of sodium sulphate. The final conclusion drawn is that the most probable value of  $k_2$  is 0.017. Sulphuric acid of less than 0.041*N* strength contains the ions  $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$ , but other ions are formed in stronger solutions. The first stage dissociations of sulphuric acid and of sodium hydrogen sulphate are almost the same as those of hydrochloric acid and of sodium chloride.

T. E.

**Conductivity of Aqueous Solutions of Sodium Chloride, Hydrochloric Acid, and their Mixtures.** WILLIAM C. BRAY and FRANKLIN L. HUNT (*J. Amer. Chem. Soc.*, 1911, 33, 781—795).—This work was undertaken in order to study, for two salts of widely different conductivities, the validity of the method of calculating the specific conductivity of mixtures of salts with a common ion which is based on the principle that the degree of ionisation of each salt in such a mixture is equal to that which it has when present alone in a solution of the same total ion concentration (compare Mackay, this vol., ii, 366).

The conductivity has been determined at 25° of 0.001—0.2*N*-solutions of sodium chloride and of hydrochloric acid, and of mixtures of these substances in which the concentrations were varied systematically. The specific conductivities of the mixtures were calculated by the rule to which reference has already been made. It is shown that large variations in the degrees of ionisation produce scarcely any change in the calculated specific conductivities, provided that the conductance of each ion is assumed to depend on the total equivalent ion concentration.

The specific conductivities calculated in this way were in all cases greater than the values obtained experimentally. The difference is about 1.6% of the actual specific conductivity when the concentration of each substance is 0.1*N* in the mixture, and is less at lower concentrations. It is suggested that the conductance of an ion may depend on its actual concentration rather than on the total ion concentration, and it is shown that a satisfactory agreement can be obtained between the measured and calculated values by assuming that this is true for the hydrogen ion, and that hydrochloric acid is ionised to about the same extent as potassium chloride.

The ratio of the specific conductivities at 25° and 18° has been determined for 0.01*N*-potassium chloride, 0.05*N*-hydrochloric acid, and for sodium chloride solutions of concentrations from 0.001*N* to 0.1*N*. The results for the potassium chloride and hydrochloric acid solutions agree with those recorded by Déguisne, but those for the sodium chloride solutions are about 0.15% higher.

E. G.

**Conductivity and Ionisation of Certain Salts at 18° and 25°.** FRANKLIN L. HUNT (*J. Amer. Chem. Soc.*, 1911, 33, 795—803).—It has been shown by Noyes (*Abstr.*, 1908, ii, 348) that the empirical dilution law  $(C\gamma)^n/C(1-\gamma) = \text{a constant}$ , in which  $n$  has values varying between 1.4 and 1.6, holds closely for dilute aqueous solutions of salts of different types over a wide range of temperature. In continuation of this work, the conductivity and ionisation at 18° and 25° have been determined of solutions of potassium and lead bromates, silver

and thallous sulphates, magnesium nitrate, lead chloride, and sulphuric acid.

When the empirical dilution law holds over a definite range of concentration for some value of  $n$ , the curve obtained on plotting  $1/\Lambda$  against  $(CA)^{n-1}$ , where  $\Lambda$  is the equivalent conductivity, must be a straight line. The results of the experiments have been plotted in this way, and the curves for each salt are found to be closely similar at  $18^\circ$  and  $25^\circ$ . By means of these curves, the value of  $n$  was chosen which gave the best straight line over any range of concentrations. Probable values of  $\Lambda_0$  at  $18^\circ$  and  $25^\circ$  were then calculated, and these agreed well with the final values except in the case of lead chloride.

The degrees of ionisation of the uni-bivalent salts decrease in the same order as the values of  $n$  increase. The value of  $n$  is high for lead chloride, and this salt is less ionised than the other salts. The values of the equivalent conductivity and the percentage ionisation of the salts are given at various concentrations. The degree of ionisation of each salt at  $25^\circ$  is rather less than at  $18^\circ$ , but the difference decreases with decreasing concentration, and is almost negligible for very dilute solutions. The degree of ionisation is almost the same for magnesium nitrate and chloride, and for potassium bromate and nitrate. It is slightly less for barium bromate than for barium nitrate, and for thallous sulphate than for silver sulphate. Thallous and silver sulphates are somewhat less ionised than lead nitrate, and these salts are all much less ionised than most other uni-bivalent salts. Lead and cadmium chlorides are still less ionised. The silver, thallous, lead, and cadmium salts evidently occupy a position intermediate between typical strong electrolytes and weak electrolytes, such as mercuric chloride.

E. G.

**Conductivity and Dissociation of Organic Acids in Aqueous Solution between  $0^\circ$  and  $35^\circ$ .** E. P. WIGHTMAN and HARRY C. JONES (*Amer. Chem. J.*, 1911, 43, 56—112).—In continuation of the work of White and Jones (*Abstr.*, 1910, ii, 821) the electrical conductivity and dissociation of a further number of organic acids have been determined from  $0^\circ$  to  $35^\circ$ . The conclusions drawn from the earlier work are confirmed, and in addition it is shown that for weak acids which are not hydrated the temperature-coefficients of conductivity increase rapidly with dilution and decrease rapidly with rise in temperature. When the acids are hydrated, the temperature-coefficients of conductivity are larger, and are less affected by dilution and alteration of temperature. Organic acids with the largest dissociation constants have also the largest temperature-coefficients of conductivity. The strong organic acids (for example, benzenesulphonic acid) do not obey the Ostwald dilution law.

The acids which have been investigated consist mainly of substituted fatty acids and substituted benzoic acids. The experimental data are quoted in detail.

G. S.

**Electrical Conductivities of Solutions in Acetic and Propionic Acids.** AL. N. SACHANOFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 526—534. Compare *Abstr.*, 1910, ii, 1027; this vol., ii, 247).—The author has measured the molecular conductivities at



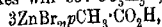
25° of solutions of various dilutions of aniline, dimethylaniline, pyridine, quinoline, dimethylpyrone, water, acetanilide, lithium and zinc bromides, and calcium and zinc iodides in acetic acid (dielectric constant, 6.46) (compare Patten, Abstr., 1903, ii, 57); and of aniline, pyridine, quinoline, and lithium bromide in propionic acid (dielectric const. 3.15). Solutions of the organic acids, even of trichloro- or tribromo-acetic acids in acetic or propionic acids, exhibit no conductivity.

The specific conductivities found for solutions of aniline, dimethyl-aniline, and quinoline in acetic acid agree with those given by Patten (*loc. cit.*), who, however, gives a higher value for pyridine solutions than is found by the author; the pyridine used by the latter boiled within 0.7°, and that used by Patten within 3°.

With the majority of the solutions examined, the conductivity does not change with lapse of time. Although in solutions of aniline in acetic acid, acetanilide and water (which are found to conduct but slightly) are gradually formed, yet this reaction is so slow at 25° that some days are necessary for the conductivity to fall by a few per cent.; this result confirms Menshutkin's observations on the velocity of formation of acetanilide (Abstr., 1882, 1084). Still slower should be the reaction between aniline and propionic acid, but here another change, accompanied by increase of the conductivity, takes place, and the same is the case with solutions of quinoline (but not of pyridine) in propionic acid; all these changes are, however, slow.

All the solutions in acetic and propionic acids examined show diminution of conductivity on dilution; this is very marked with the more concentrated solutions, and gradually becomes less and less so as the dilution increases.

The probable cause of these anomalies is the formation of complex conducting compounds (compare Steele, McIntosh, and Archibald, *Zeitsch. physikal. Chem.*, 1906, 55, 183), and this is confirmed by the observation that acetic acid favours the formation of complex compounds in a high degree; indeed, many salts undergo polymerisation in this solvent. If the formula of the complex compound capable of electrolytic dissociation is  $mA, pB$  (where  $A$  and  $B$  represent a mol. of the solute and solvent respectively), then the function  $KV^m$  ( $K$  being the specific conductivity, and  $V$  the dilution) should increase with dilution like the molecular conductivity ( $KV$ ) of aqueous solutions. For many solutions in acetic acid, this function will be  $KV^3$ , so that the formulae of the complexes will be:  $3C_6H_5N, pCH_3 \cdot CO_2H$ ;



etc.;  $p$  remains undetermined, but is probably greater than unity.

For solutions of dimethylpyrone, lithium bromide, and calcium iodide in acetic acid, the function  $KV^2$  already increases with the dilution, the complexes being therefore:  $2C_6H_5O, pCH_3 \cdot CO_2H$ ;  $2LiBr, pCH_3 \cdot CO_2H$ , etc.

Solutions in propionic acid exhibit considerably more rapid diminution of the molecular conductivity on dilution than those in acetic acid, so that  $m$  is greater than 3; but the determination of the value of  $m$  necessary for the function  $KV^m$  to increase with dilution is impossible in this case, as the theory developed by Steele, McIntosh, and Archibald

is applicable solely to relatively dilute solutions, whilst only the more concentrated solutions in propionic acid exhibit conductivity. This theory finds confirmation in the change in the conductivity of acetic and propionic acid solutions with change of temperature (compare following abstract).

The dielectric constant of propionic acid is very small, being less than that of either chloroform (4.95) or ether (4.37), but, in spite of this, concentrated solutions of aniline, pyridine, or lithium bromide in this acid are conducting; in isoamyl acetate (diel. const. 4.79), lithium bromide shows very slight conductivity, whilst solutions in dimethylaniline are insulators (Patten, *loc. cit.*). On the other hand, amylamine (dielect. const. 4.5) approaches propionic acid in the conductivity of its solutions (compare Kahlenberg and Ruhoff, *Abstr.*, 1903, ii, 464), and in the rapidity with which the molecular conductivity falls on dilution.

The dielectric constant of ethyl benzoate (6.62) is almost equal to that of acetic acid; yet a solution of lithium bromide in the latter conducts some hundreds of times as well as one of equal dilution in the former solvent; solutions of calcium and zinc iodides in these two solvents show similar relations. The conductivities of organic bases and of potassium acetate in acetic acid are so high that, in concentrated solutions, they exceed the conductivity of acetic acid in water. Like propionic acid, acetic acid gives solutions approximating in conductivity to those in primary amines with similar dielectric constants, *e.g.*, aniline and ethylamine (compare Shinn, *Abstr.*, 1907, ii, 926).

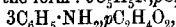
These results confirm the inapplicability of the Nernst-Thomson law to solvents with low dielectric constants, and indicate that the principal factor governing their dissociating power is their chemical nature.

T. H. P.

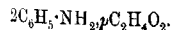
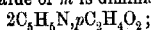
**Abnormal Conductivity Changes.** AL. N. SACHANOFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 534—546).—The author has further examined solutions in acetic and propionic acids (see preceding abstract) in order to test the sufficiency of Steele, McIntosh and Archibald's theory (*Zeitsch. physikal. Chem.*, 1906, 55, 179; *Abstr.*, 1907, ii, 840) to account for the anomalous changes in the conductivity of such solutions.

The results show that at 100° the number of molecules of the solute (*m*) entering into the composition of the complex molecule is less than at 25°, this being the cause of the characteristic difference between the molecular conductivity curves at 100° and at 25°. The molecular conductivity at 100° changes less by far than that at 25° on dilution; the relative change of conductivity from 25° to 100° is different for solutions of different concentrations.

At 25° the complex compounds conducting the current in acetic acid solutions will be of the form:  $3C_6H_5N, pC_2H_4O_2$ ;



etc., whilst at 100° the value of *m* is diminished to two:



T. H. P.

**Influence of Alkyl Substituents on the Electrical Conductivity of Malonic Acid.** WILLIAM B. MELDRUM (*J. Physical Chem.*, 1911, 15, 474—488. Compare Walker, *Trans.*, 1892, 81, 696).—The conductivity of 18 mono- and di-alkyl substituted malonic acids was determined, and the monobasic dissociation constants were calculated by Ostwald's formula. These results combined with those of Walden (1891) enable the following conclusions to be drawn. The introduction of one alkyl group into malonic acid decreases the dissociation, this influence being greatest for the methyl and least for the ethyl group. *n*-Propyl and *n*-butyl produce an intermediate effect. The *iso*alkyl malonic acids are usually more dissociated than the corresponding normal compounds. The *isobutyl* group has an abnormal influence, lowering the constant considerably when alone and raising it when in conjunction with other groups.

The introduction of a second alkyl group into a monoalkylmalonic acid is accompanied by an increase in the dissociation above that of malonic acid, except in the case of two methyl groups.

It is suggested that one alkyl group diminishes the reinforcing influence of the carboxyl groups on each other, whereas a second alkyl group serves to bring the two carboxyls into close proximity again.

R. J. C.

**Conductibility Accompanying Chemical Reactions.** G. REBOUL (*Compt. rend.*, 1911, 152, 1660—1661).—The reactions examined were allowed to proceed in such a way that there was but little surface disturbance and only slight rise in temperature. For this purpose, chlorine diluted by an inert gas was passed over sodium, antimony, copper amalgam, etc. In no instance was there a marked production of ions.

W. O. W.

**Electrical Induction in Chemical Reactions.** L. G. WINSTON (*Amer. Chem. J.*, 1911, 45, 547—553).—A discussion is given of the mechanism of chemical reactions based on the conception of electrostatic induction, the rearrangement of the atoms being compared with the distribution of positive and negative electricity in a neutral body by induction. The conditions best suited for induction are found in organic chemistry, and the hypothesis is applied to the explanation of the formation of homologous compounds by the substitution of a radicle for a hydrogen atom, and to the elucidation of tautomeric changes, the formation of polymerides, and the function of a catalyst.

E. G.

**Elimination of Liquid Potentials in Measurements of Electrode Potentials.** NIELS BJERRUM [and, in part, (Erl.) J. BJERRUM] (*Zeitsch. Elektrochem.*, 1911, 17, 389—393).—Liquid potentials may be calculated with greater accuracy by Henderson's theory than by that of Planck (this vol., ii, 182). The former theory indicates that when a solution of potassium chloride is used to separate two dilute solutions, the liquid potential is the sum of two parts, one of which is due to the unequal mobilities of potassium and chlorine ions, and the other to the unequal mobilities of the anions

and cations of the dilute solutions. The latter portion is almost twice as great with a half-saturated solution of potassium chloride as it is with a saturated solution, whereas the first portion is approximately the same. By making two measurements with the two solutions of potassium chloride and extrapolating, the variable potential may be eliminated; the constant part must be calculated. In examples given it varies from  $-0.18$  to  $+0.72$  millivolt. A solution of ammonium nitrate gives larger values for this constant potential, owing to the greater difference in the mobilities of the ions. These conclusions are confirmed by a number of measurements.

T. E.

**Selfinduction with the Semi-insulator in Relation to Concentration Cells.** CHARLES M. VAN DEVENTER (*Chem. Weekblad*, 1911, 8, 468—472. Compare van Deventer and van Lummel, *Abstr.*, 1908, ii, 12, 558).—A contribution to the author's theory of the "leaking insulator."

A. J. W.

**Electrochemistry of Hydronitric Acid [Azoimide] and its Salts. I. Corrosion of Some Metals in Sodium Trinitride Solution.** J. W. TURBENTINE (*J. Amer. Chem. Soc.*, 1911, 33, 803—828).—A study has been undertaken of the electrochemical behaviour of azoimide and its salts (the trinitrides) with special reference to the relation of the  $N_3$  ion to other ions. In the present paper, an account is given of the electrochemical corrosion of magnesium, aluminium, zinc, iron, nickel, tin, lead, cadmium, copper, and silver in sodium azoimide solution. The experiments were made with each metal in both unstirred and stirred solution. The electrolytic bath was a 2% solution of sodium azoimide, and the cathodes usually consisted of platinum wires. The anodes were weighed before the experiment, and after they had been subjected to corrosion were cleaned, dried, and again weighed.

In the case of magnesium, the results show that the electrochemical equivalent of this metal is twice as great as would be expected in accordance with Faraday's law. Aluminium, zinc, and cadmium also give anode efficiencies of considerably more than 100%. In order to explain these phenomena, it is suggested that the metals dissolve electrochemically at a valency lower than that usually assigned to them with formation of compounds which are readily oxidised. This hypothesis is supported by the fact that reduction products of the  $N_3$  ion, such as ammonia, hydrazine, and nitrogen, are found in the region of the anode, the presence of which indicates that some reducing agent is formed at the anode. As an example of the change which occurs, reference may be made to the behaviour of magnesium. It is supposed that magnesian azoimide,  $MgN_3$ , is formed at the anode, and that this causes the reduction of the azoimide ion with formation of ammonia, hydrazine, and nitrogen in accordance with the equation:  $8MgN_3 + 10H_2O = 3MgN_2 + 5Mg(OH)_2 + 2NH_3 + N_2H_4 + N_2$ .

Nickel and lead become passive in unstirred solutions, whilst aluminium, iron, nickel, tin, lead, and silver become passive, or nearly so, in stirred solutions.

E. G.

**An Electrical Tungsten-resistance Oven for Chemical Purposes.** FRANZ FISCHER and ERICH TIEDE (*Ber.*, 1911, 44, 1717—1720).—The oven is very similar in principle to that described by Pring and Hutton (*Trans.*, 1906, 89, 1591) and Greenwood (*Trans.*, 1908, 93, 1483), except that the resistance of carbon or iridium is replaced by a tube formed from compressed tungsten, the upper part of the centre of the tube being cut away to form a hollow for holding a magnesia crucible. Surrounding the resistance is a glass globe, connected with a Gaede mercury pump, and kept cool by a continuous stream of cold water flowing over it.

With the above apparatus, 1.5 grams of tin could be distilled in five minutes, the tungsten tube being heated to near its vaporising temperature. The tin collected partly on the edge of the magnesia crucible, and partly as a black mirror on the cool surface of the glass globe.

T. S. P.

**Researches on Magnetism. III. Para- and Dia-magnetism at Very Low Temperatures.** H. KAMERLINGH ONNES and ALBERT PERRIER (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 115—122).—Measurements of the magnetic susceptibility of gadolinium sulphate, ferrous sulphate, dysprosium oxide, and electrolytic bismuth have been made at temperatures ranging from room temperature down to 14° abs. In the case of gadolinium sulphate, the product of specific susceptibility and absolute temperature is constant down to 17° abs. in accordance with Curie's law. A slight diminution in the value of the product is found at 14° abs.

For ferrous sulphate, Curie's law is satisfied down to 64° abs., but at lower temperatures, deviations are found which increase in magnitude as the temperature falls. In the case of dysprosium oxide, the temperature susceptibility product begins to exhibit divergences at 170° abs., and at liquid hydrogen temperatures the susceptibility is only about half what it should be according to Curie's law. Between 20° and 14° abs. the susceptibility varies inversely as the square-root of the absolute temperature, which relationship was also found for liquid oxygen at temperatures between 90° and 63° abs. It is probable therefore that this behaviour is characteristic of all substances for a certain temperature range.

The data for bismuth show that the linear relationship between the susceptibility and the temperature, which has been found at higher temperatures, ceases to be valid at very low temperatures. At liquid hydrogen temperatures the susceptibility is nearly independent of the temperature.

H. M. D.

**Rationality of the Proportions of the Molecular Magnetic Moments and the Magneton.** PIERRE WEISS (*Arch. Sci. phys. nat.*, 1911, [iv], 31, 401—438).—By application of Langevin's kinetic theory of dia- and para-magnetism to the magnetisation data for para- and ferro-magnetic solids and for dissolved para-magnetic substances, it is found that the magnetic moment of an element varies in such a way that the several values can be represented by simple ratios. For different elements, the magnetic moments are also related in a simple

manner, and these facts lead the author to put forward the hypothesis that magnetisation is of atomic character. The indivisible elementary magnetic unit is termed a magneton. This is supposed to be a constituent of the atoms of all elements. The elements, for which available magnetisation data indicate the validity of the magneton hypothesis, are iron, nickel, cobalt, chromium, manganese, vanadium, copper, mercury, uranium, and the metals of the rare earths. From observations on the magnetisation of iron and nickel at the temperature of liquid hydrogen and Perrin's value for the number of atoms in a gram-atom of an element ( $68.5 \times 10^{-22}$ ), the author calculates the moment of the elementary magneton to be  $16.4 \times 10^{-22}$ .

H. M. D.

**Specific Heat of Different Gases and Vapours.** R. THIBAUT (*Ann. Physik*, 1911, [iv], 35, 347—377).—The sound-wave method of determining  $k = C_p/C_v$  described by Behn and Geiger (Abstr., 1908, ii, 99) has been used to determine the specific heat of carbon dioxide, hydrogen sulphide, sulphur dioxide, carbon disulphide, and ethyl ether at room temperature. Measurements of the heat capacity of the vapours of benzene, methyl alcohol, ethyl alcohol, and chloroform at about  $350^\circ$  have also been made by the differential calorimetric method described by Nernst (*Zeitsch. Elektrochem.*, 1910, 16, 96).

The sound-wave method is unsuitable in the case of gases or vapours for which  $C_p$  is very large. At high temperatures,  $C_p$  increases as the number of atoms in the molecule increases, and for gases which contain the same number of atoms in the molecule it increases with the molecular weight. With rise of temperature,  $C_p$  increases more quickly as the ratio of the number of atoms in the molecule to the molecular weight increases. Carbon dioxide and sulphur dioxide have approximately the same molecular heat; this is also the case for water and hydrogen sulphide, but there is a considerable difference between the values for carbon dioxide and carbon disulphide. In the case of carbon dioxide, sulphur dioxide, and hydrogen sulphide, the specific heat ratio differs appreciably according to whether the measurement is made at a pressure of 1 or  $\frac{1}{2}$  atmosphere.

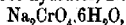
H. M. D.

**Transition Temperatures of Sodium Chromate as Convenient Fixed Points in Thermometry.** THEODORE W. RICHARDS and GEORGE LESLIE KELLEY (*J. Amer. Chem. Soc.*, 1911, 33, 847—863).—In earlier papers (Richards and Churchill, Abstr., 1898, ii, 555; 1899, ii, 354; Richards and Wells, Abstr., 1903, ii, 411; 1906, ii, 727; and Richards and Wrede, Abstr., 1908, ii, 16), it has been shown that the transition temperatures of certain crystallised salts, such as sodium sulphate, sodium bromide, and manganous chloride, can be so easily observed and constantly maintained as to form convenient fixed points in thermometry.

Sodium chromate has now been studied from this point of view and is regarded as of particular value, since it has three transition temperatures in the neighbourhood of  $20^\circ$ , a temperature at which thermometers frequently need to be verified.

Pure sodium chromate can be prepared by treating pure recrystallised sodium dichromate with rather less than the calculated quantity of sodium carbonate and completing the neutralisation by means of sodium hydroxide solution with the aid of phenolphthalein.

The existence of the three hydrates,  $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$ ;



and  $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$ , has been confirmed. The points at which each of these hydrates is converted into each of the other two can be accurately determined. The addition of heteromorphous substances lowers the transition temperatures as usual. Successive additions of sodium sulphate (which yields an isomorphous decahydrate) cause successive elevations of the transition temperature of the decahydrate-hexahydrate which are roughly proportional to the amounts added. In some cases an elevation of about  $4^\circ$  was observed. The transition temperatures, on the international hydrogen scale, are approximately, as follows: decahydrate-hexahydrate,  $19.525^\circ$ ; decahydrate-tetrahydrate,  $19.987^\circ$ ; hexahydrate-tetrahydrate,  $25.90^\circ$ . E. G.

**Fusibility Curves of Gaseous Mixtures: Systems Formed by Carbon Dioxide and Hydrogen Sulphide with Methyl Alcohol and Methyl Ether.** GEORGES BAUME and F. LOUIS PERROT (*Comp. rend.*, 1911, 152, 1763—1765. Compare Abstr., 1909, ii, 545; 1910, ii, 825; this vol., i, 414).—The fusibility curves of carbon dioxide with methyl ether or methyl alcohol, and of the latter with hydrogen sulphide show no maxima. That of the system methyl ether-hydrogen sulphide has a distinct maximum at  $-148.5^\circ$ , corresponding with the compound  $\text{OMe}_{20}\text{H}_2\text{S}$ . The curves are reproduced in the original paper, which also contains a diagram of the apparatus employed.

W. O. W.

**Influence of Pressure on the Melting Points of Certain Metals.** JOHN JOHNSTON and L. H. ADAMS (*Amer. J. Sci.*, 1911, [iv], 31, 501—517).—An apparatus is described by means of which chemical and physical changes can be investigated at temperatures up to  $400^\circ$  and under pressures up to 2000 atmospheres. This apparatus has been used to determine the influence of pressure on the melting point of tin, bismuth, lead, and cadmium. Up to 2000 atmospheres, the melting point varies with the pressure according to a linear equation. The rise of temperature per atmosphere was found to be as follows: tin  $0.003275^\circ$ , cadmium  $0.006288^\circ$ , lead  $0.008026^\circ$ . In the case of bismuth the melting point falls to the extent of  $0.003548^\circ$  per atmosphere. The measured changes of the melting point with pressure are shown to be in satisfactory agreement with the values calculated from the respective latent heats of fusion and the volume changes which occur on melting. The melting points at atmospheric pressure were determined both with copper-constantan and platinum-platinum rhodium couples, and found to be: tin  $231.0^\circ$ , bismuth  $270.7^\circ$ , cadmium  $320.4^\circ$ , and lead  $326.7^\circ$ . These temperatures refer to a scale obtained by measurements of the boiling points of naphthalene and benzophenone and the melting point of zinc. H. M. D.

**Determination of Melting Points of Crystalline Liquids.** H. STOLTZENBERG (*Zeitsch. physikal. Chem.*, 1911, 77, 73—74).—Into the melting-point tube a glass rod, bent horizontally at the upper end, is inserted, and in the capillary layer thus formed between rod and tube, melting points of crystalline liquids can be observed very sharply. Further, in such a tube alterations in the height of the meniscus connected with transitions from one phase to another can readily be observed.

G. S.

**Molecular Complexity of Salts in Phenol.** CURT B. HARTUNG (*Zeitsch. physikal. Chem.*, 1911, 77, 82—90).—The molecular weights of sodium acetate, aniline and dimethylamine hydrochlorides, tetramethylammonium iodide and the potassium and rubidium salts of oximinodiketohydrindene (a weak acid) in phenol have been determined by the cryoscopic method in different dilutions. The salts of the two weak acids show an abnormally great molecular depression in  $N/10$ -solution, which cannot be due to electrolytic dissociation, as in the same dilution the  $i$  value for tetramethylammonium iodide is nearly unity. The results are ascribed to "phenolysis" of the salts, analogous to hydrolysis. The curve obtained for the two salts of oximinodiketohydrindene by plotting  $i$  values as ordinates against dilutions as abscissæ show distinct minima, a result which is ascribed to association between solute and solvent with a consequent diminution of "free" solvent, which is of importance in concentrated solution.

G. S.

**Method for Determining Heat of Evaporation as Applied to Water.** THEODORE W. RICHARDS and J. HOWARD MATHEWS (*J. Amer. Chem. Soc.*, 1911, 33, 863—888).—The recorded values of heats of vaporisation of various liquids are very discordant, owing partly to the use of impure materials and partly to the employment of faulty methods. A satisfactory method has now been devised, and is fully described. A modification of Kahlenberg's form of Berthelot's apparatus is employed in conjunction with the adiabatic method of calorimetry (*Abstr.*, 1905, ii, 677; 1907, ii, 604; 1908, ii, 806; 1910, ii, 391, 930) and the use of a Dewar vessel as vaporiser.

It has been found that a serious error, amounting to about 0.1% of the total per minute, is caused by premature condensation in the narrow zone between the vaporiser and the condenser. This error was reduced as far as possible by modifications in the apparatus, and was finally eliminated by conducting experiments at different rates and extrapolating the results to a hypothetical instantaneous experiment in which the disturbing effect may be regarded as zero.

The heat of vaporisation of a gram of water was found to be 538.9 Cal.<sub>25°</sub>, or 2.251 kilojoules per gram. A gram-molecule therefore requires 9.707 Cal.<sub>25°</sub> or 40.54 kilojoules when the vaporisation is carried out at 100° ( $0 = 16.000$ , 1 Cal.<sub>25°</sub> = 4.177 kilojoules). This result compares satisfactorily with those of previous investigators, and proves that the method is trustworthy and suitable for general use.

The method has been applied to other liquids, and has given concordant results.

E. G.



The Specific Gravities of the Elements Considered in their Relation to the Periodic System. ARTHUR JOHN HOPKINS (*J. Amer. Chem. Soc.*, 1911, 33, 1005—1037).—The relationships between atomic weights, densities, specific volumes, atomic volumes, and position numbers in the periods are discussed, and the view put forward that the position number is the fundamental property of an element, the density, valence, and all properties dependent on these being functions of the position number. A slightly modified arrangement of the periodic system is suggested in the second part of the paper.

H. M. D.

Relation of Vapour Pressure to Specific Gravity in Binary Liquid Mixtures. ANTONY G. DOROSCHIEWSKY (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 656—670).—In discussing the relation of the vapour pressure ( $P$ ) of a mixture of two liquids to the specific gravity, the author compares the deviation  $dP$  of the actual vapour pressure from the value calculated according to a straight line law with the corresponding deviation (contraction)  $dV$  for the volume of the mixture. It is known (Young, *Trans.*, 1902, 768; Kuenen, "Theorie der Verdampfung und Verflüssigung," 1906, 137) that, for liquids which have a straight line vapour pressure curve, the contraction (and the heat effect of mixing) is very small, so that when  $dP=0$ ,  $dV$  approaches 0; as the contraction was determined at an appreciably lower temperature than the vapour pressure, it may be that, at identical temperatures, when  $dP=0$ ,  $dV$  also = 0.

Kuenen regards mixtures of methyl and ethyl alcohols as having a rectilinear vapour pressure curve, but calculation by means of Raywood's results (*Abstr.*, 1900, ii, 64) shows that the straight line value is greater than the experimental by an amount almost constant for all solutions, namely, 29 mm.

Consideration of the somewhat insufficient data available points to the conclusion that when  $dP$  is zero,  $dV$  is zero, and when  $dP$  is constant,  $dV$  is also constant. Further, a maximum or minimum value of  $dP$  corresponds with a maximum or minimum value of  $dV$ .

The mixtures showing the most regular relations between  $dP$  and  $dV$  are those of ethyl alcohol and water, probably owing to the fact that they have been more completely and accurately studied than others.

The connexion between  $dP$  and  $dV$  is manifested in a general way, but there are certain peculiarities of  $dP$  for which no peculiarities of  $dV$  exist. Thus, in cases where a maximum of vapour pressure is not very well defined, for example, in mixtures of ethyl alcohol and water, the contraction curve shows no peculiarity at a corresponding point.

The conclusion is drawn that a maximum vapour pressure indicates a special molecular process in the solution.

T. H. P.

The Weight of a Falling Drop and the Laws of Tate. VII. The Drop Weights of Some of the Lower Esters and the Surface Tensions and Molecular Weights Calculated from Them. J. LIVINGSTON R. MORGAN and FREDERICK W. SCHWARTZ (*J. Amer. Chem. Soc.*, 1911, 33, 1041—1060. Compare *Abstr.*, 1908, ii, 356, 668; this vol., ii, 372, 584, 585).—The drop weight method of

determining surface tension has been applied to various esters of the lower fatty acids with a view of comparing the results with those obtained by the method of capillary rise. In general, the agreement is quite satisfactory, but deviations are found in the use of methyl formate, amyl formate, and ethyl acetate.

When the equation  $w(M/d)^{1/2} = k_d(t_o - t - 6)$  is applied to the drop weight data with the object of finding a value of  $t_o$  which is independent of the temperature of observation  $t$ , using, in all cases, the value of  $k_d$  found for benzene ( $t_o = 288.5^\circ$ ), it is found that methyl acetate, ethyl acetate, propyl acetate, methyl butyrate, methyl isobutyrate, methyl propionate, ethyl propionate, and amyl formate have a normal molecular weight. Only in the case of methyl acetate does the calculated  $t_o$  agree with the observed critical temperature, the calculated values being higher in all the others except methyl, ethyl, and propyl formates. In these three cases, rise of temperature appears to cause some change to take place which can be removed by sudden cooling, but persists when the cooling is effected slowly, leading to a higher drop weight than that found for the unheated liquid.

H. M. D.

**The Weight of a Falling Drop and the Laws of Tate.** VIII. The Relationship Existing between the Weight of the Drop, the Diameter of the Tip from which it Falls, and the Surface Tension of the Liquid. J. LIVINGSTON R. MORGAN and JESSIE Y. CANN (*J. Amer. Chem. Soc.*, 1911, 33, 1060—1071. Compare preceding abstract).—The weights of falling drops of benzene, quinoline, pyridine, ethyl ether, and carbon tetrachloride have been determined at  $27.8^\circ$ , using sixteen different tips varying in diameter from 3.05 to 7.86 mm. In the case of the smaller and larger tips, the drop formation is abnormal, and values are obtained for the drop weights which are too large. All liquids are found to give satisfactory results with a tip of 4.5 mm. diameter, and if liquids, like carbon tetrachloride, which have a very small surface tension and large density are excluded, equally good results are obtained by the use of tips with diameters between 4.5 and 5.5 mm. The general conclusion which the authors draw from these measurements is that the weight of a falling drop is rigidly proportional to the diameter of the tip from which it falls, if the drop formation is not visibly abnormal.

H. M. D.

**The Compression of Liquids at High Pressures.** (Hon.) CHARLES A. PARSONS and S. S. COOK (*Proc. Roy. Soc.*, 1911, A, 85, 332—348).—The compressibility of water, ethyl ether, paraffin, and graphite has been measured by means of an apparatus in which the pressure could be raised to more than 6000 atmospheres. This apparatus consisted of a gun steel mould, placed under a heavy hydraulic press, water being supplied to the upper side of the ram by a three-throw hydraulic pump driven by an electric motor. The pressure on the ram was recorded by a Bourdon gauge, and the depression of the liquid in the mould was measured by a pair of multiplying callipers.

The following isothermal coefficients of compressibility were obtained for pressures of 1, 2000, and 4500 atmospheres respectively: water (4°) 50, 25, and  $22.5 \times 10^{-6}$ ; ethyl ether (35°) 165, 42.5, and  $18 \times 10^{-6}$ ; paraffin oil (34°) 87, 34, and  $17 \times 10^{-6}$ .

Measurements of the cooling effect produced by adiabatic expansion were also made, and from these the authors calculate the magnitude of the internal pressure. For water this is 2150 atmospheres, for ethyl ether 2440, and for paraffin 2920.

The experiments with Atchison and Ceylon graphite indicate that this does not behave as a fluid under high pressures, but that it attains a greater degree of consolidation as the pressure increases. By immersing the graphite in water, its bulk compressibility was found to be about  $6.5 \times 10^{-6}$  in atmospheric units.

H. M. D.

**The Adsorption of Some Substances by Starches.** HOVES LLOYD (*J. Amer. Chem. Soc.*, 1911, 33, 1213—1226).—The adsorption of hydrogen chloride, sodium chloride, and sodium hydroxide from aqueous solution by cassava, arrowroot, potato, rice, and maize starch granules has been investigated. The rapidity with which equilibrium is attained indicates that the effect is one of adsorption. With 50 grams of starch and 100 c.c. of solution, five minutes' stirring was found to suffice for the completion of adsorption. The influence of temperature is very small, and on this account the experiments could be carried out at room temperature.

The adsorption of the three electrolytes varies with the different starches, but not nearly so much as might be expected, considering the great differences in the size of the granules. Sodium hydroxide is adsorbed to a much greater extent than either hydrogen or sodium chloride. In the case of hydrogen chloride, adsorption takes place in accordance with the exponential adsorption formula up to a concentration of 0.4*N*. Within this range divergent results were, however, obtained when maize starch granules were employed.

H. M. D.

**The Dissociation Equilibrium  $S_8 \rightleftharpoons 4S_2$ .** O. J. STAFFORD and H. VON WARTENBERG (*Zeitsch. physikal. Chem.*, 1911, 77, 66—74).—When heat is conveyed between two surfaces at different temperatures through a dissociating gas, the thermal conductivity should be much higher than for a non-dissociating gas, since, in the former case, dissociation is taking place at the hot wall and re-combination at the cold wall, and therefore an extra transport of heat due to the heat of dissociation occurs. The authors have used this principle in order to settle the question whether any intermediate stages (for example,  $S_6$ ) occur in the dissociation  $S_8 \rightarrow 4S_2$ . As a matter of fact, the curve obtained by plotting the thermal conductivity as ordinates against the temperatures as abscissæ shows one pronounced maximum only, and this at first sight appears to show that only the molecules  $S_8$  and  $S_2$  are present. This is opposed to the results of Preuner and Schupp (compare Abstr., 1910, ii, 118), and the authors point out that in this curve there is a rapid alteration in the molecular complexity with temperature, so that the different maxima which might be anticipated

for the various stages of the dissociation have coalesced to a single maximum. Bearing in mind this limitation, the measurement of the thermal conductivity is a useful method for determining the condition of a dissociating gas.

G. S.

**Measurement of Surface Tension by the Method of Capillary Rise.** JULES E. VERSCHAFFELT and (Mlle.) L. VAN DER NOOT (*Bull. Acad. roy. Belg.*, 1911, 5, 383—394).—It is shown that the variation of the capillary rise and the form of the capillary surface with the radius of the tube is such that it may be represented in each case by a single curve applicable to all liquids. For this purpose the curves must be plotted on a scale which is proportional to  $1/a$ ,  $a^2$  being the capillary constant of the liquid.

Measurements of the capillary rise of water, benzene, ethyl ether, and carbon disulphide have been made in tubes of radius varying from 0.094 to 1.56 mm., and the data are shown to be in agreement with the above deduction. A similar result is found in respect of the form of the capillary meniscus for the same liquids.

H. M. D.

**Relation of Osmotic Pressure to Temperature. V. The Measurements.** HARMON N. MORSE, WILLIAM W. HOLLAND, E. G. ZIES, C. N. MYERS, W. M. CLARK, and E. E. GILL (*Amer. Chem. J.*, 1911, 45, 554—603. Compare this vol., ii, 191, 375, 473).—An account is given of a series of determinations of the osmotic pressure of solutions of sucrose of 0.1, 0.2, 0.3, 0.4, and 0.5 weight-normal concentration at 0°, 5°, 10°, 15°, 20°, and 25°.

In four of the determinations, membranes of nickel ferrocyanide were used instead of those of copper ferrocyanide, and behaved in a satisfactory manner.

The rotatory power of the solutions remained constant in all the experiments recorded, and it is therefore evident that none of them were vitiated by leakage through the membranes, and that no inversion of the sucrose occurred in the cells. In one experiment, a cell maintained the concentration of the solution and the consequent osmotic pressure for more than eight weeks. This demonstrates the durability of the membranes, and shows that it is not necessary to stir the solutions. It also proves that osmotically active membranes may be made truly semi-permeable. The temperature of the solutions did not usually fluctuate more than 0.01°, and in no case more than 0.02°.

The ratio of osmotic pressure to gas pressure is constant for each concentration. This ratio in the 0.1*N*-solution was 1.082—1.084 at 5°, 10°, 15°, 20°, and 25°, but at 0° was 1.106, the osmotic pressure being higher at 0° than at 5°. It is pointed out in this connexion that at 0° the 0.1*N*-solution is within less than 0.2° of its f. p.

The conclusion is drawn from these experiments that, if the 0.1*N*-solution at 0° is excepted, the osmotic pressures of all solutions containing from 0.1 to 1.0 gram-mol. of sucrose per litre of water obey Gay-Lussac's law between 0° and 25°.

E. G.

**Osmotic Phenomena in Non-conducting Media.** PAUL BARY (*Compt. rend.*, 1911, 152, 1766—1767. Compare this vol., ii, 590).—A rubber membrane vulcanised with sulphur chloride is semi-permeable towards a solution of sulphur in benzene, and, in general, permeable towards substances dissolved in liquids capable of swelling the material. If a porous vessel containing a solution of acetylcellulose in tetrachloroethane is surrounded with the same solvent, no transfer of liquid occurs in either direction. A substance such as hexachloroethane, which is soluble both in acetylcellulose and tetrachloroethane, will traverse the dividing septum, however. These experiments are quoted in support of the conception of colloids put forward in a previous communication, and all semi-permeable membranes are considered to be composed of colloidal materials, their permeability being proportional to the solubility of the dissolved substance in the membrane.

W. O. W.

**Osmotic Pressure of Colloids. III. Dialysis and Osmosis of Solutions of Dyes.** WILHELM BILTZ and F. PFENNING (*Zeitsch. physikal. Chem.*, 1911, 77, 91—116. Compare Abstr., 1910, ii, 22, 693).—The results of the dialysis experiments have already been published (compare this vol., ii, 375); for the conductivity and osmotic pressure measurements, orange TA extra and "cloth-red" GA, salts of monosulphonic acids; brilliant-Congo, derived from a trisulphonic acid, and Congo-blue and Chicago-blue, salts of tetrasulphonic acids, were used. They were first freed as far as possible from inorganic salts by dialysis. The conductivity measurements appear to show that they behave as normal electrolytes, the molecular conductivity in great dilution being for the monosulphonates 100—150, for the disulphonate (Congo-red) 213, for brilliant Congo 363, and for the tetrasulphonates 451—532. On the other hand, Ostwald's rule regarding the dependence of the molecular conductivity on the basicity of the acid does not apply.

The osmotic measurements were made as already described, pure water and also salt solutions being used as an exterior liquid. The results show that a dye solution is highly complicated, as products of association, electrolytic dissociation, and hydrolysis occur in equilibrium. In the monosulphonates, association and hydrolysis are of most importance, and the observed molecular weight is much higher than the calculated. With disulphonates electrolytic dissociation approximately balances association, so that the compounds appear to be unimolecular; with tri- and tetra-sulphonates, on the other hand, electrolytic dissociation is of most importance, and the observed molecular weights are smaller than the calculated. An explanation is given for the fact that, in spite of polymerisation, the monosulphonates show the normal conductivity of binary electrolytes.

G. S.

**Concentric Stratification in Filter Paper.** E. LENK and H. BRACH (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 325—326).—The formation of a precipitate in concentric rings is readily observed when a sheet of thick filter paper is moistened with a solution of potassium dichromate, and silver nitrate solution is allowed to drop slowly on to

the paper at a fixed point. The effects are quite similar to those which are obtained with solidified gelatin films, but the rings are developed much more quickly when filter paper is employed.

H. M. D.

**Weak Electrolytes, and towards a Dynamical Theory of Solutions.** WILLIAM SUTHERLAND (*Phil. Mag.*, 1911, [vi], 21, 17—66. Compare Abstr., 1902, ii, 300; 1907, ii, 599).—An attempt is made to elaborate a theory of solutions on a molecular kinetic basis. The motions of the molecules in a liquid mixture are supposed to be mutually influenced, and this has an effect on all those properties of the mixture which depend on the relations of a molecule to its immediate neighbours, such as cohesion, density, viscosity, and the like. The kinetic principle is applied to the calculation of the densities of solutions of ethyl alcohol and acetic acid in water and of the contraction which occurs in their formation. Its application to the refractivity, dielectric capacity, viscosity, specific heat, heat of solution, and surface energy in the case of mixtures of water with ethyl alcohol and the first four members of the series of fatty acids is also examined. The interpretation of the dilution law as applied to weak electrolytes is also discussed, and shown to be in agreement with the author's views. According to these, the changes in most of the physical properties which occur when ethyl alcohol or fatty acids are admixed with water are due to changes in the water itself, trihydrol being converted into dihydrol and dihydrol into hydrol. H. M. D.

**Formation of Solid Metallic Solutions by Diffusion in the Solid State.** GIUSEPPE BRUNI and D. MENEGRINI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 671—674).—Nickel and copper form solid solutions in all proportions (compare Guertler and Tammann, Abstr., 1907, ii, 174; Kurnakoff and Schentschuschny, Abstr., 1907, ii, 525), and the curve representing the conductivity as a function of concentration shows a somewhat flattened minimum corresponding with 40—60% by weight of copper.

In order to ascertain whether these alloys can be formed by diffusion of the solid metals, the authors have subjected a nickel wire, coated electrolytically with a compact covering of copper, to a temperature of about 1000° in an atmosphere of dry hydrogen, this temperature being about 80° below that at which the copper melts. The resistance of a certain length of the wire was measured from time to time. The resistance (0.026 ohm) at first diminished very slightly and subsequently increased, slowly in the beginning, then very rapidly, and finally slowly again, a constant value of about 0.21 ohm being approached. The wire showed no signs of fusion, and had the appearance and conductivity of constantan. T. H. P.

**Validity of the Boyle-Gay-Lussac Laws for Colloidal Solutions.** II. THE SVEDBERG and KATSUJI INOUE (*Zeitsch. physikal. Chem.*, 1911, 77, 145—191. Compare Abstr., 1910, ii, 772).—The validity of the laws in question has been further tested by ultra-microscopic observations with solutions of colloidal gold and of gamboge on the basis of the principles already described. The main conclusions

are as follows. The compressibility diminishes with increasing concentration and with increase in the size of the particles; in very great dilution the gas laws are accurately followed. There is a considerable deviation between the observed and calculated frequency numbers in concentrated solutions, but the agreement becomes better with increasing dilution and is ultimately exact. The influence of a number of substances, such as carbamide, sucrose, and certain electrolytes, on the compressibility has been determined; in no case does the effect exceed the limits of experimental error. Further, it is shown that the compressibility is independent of the viscosity of the dispersion medium, and Dalton's law of independent partial pressures is also valid. Finally, as the compressibility ratio is much greater for the gamboge system than for colloidal gold for the same size of particle, it follows that the compressibility depends on the nature of the disperse phase.

The experimental data are quoted in great detail.

G. S.

**Phenomena of Crystallisation in Ternary Systems. I, II, and III. Isomorphous Ternary Mixtures with a Miscibility Gap.** NICOLA PARRAVANO and G. SIROVICH (*Gazzetta*, 1911, 41, 1, 417—453, 478—489, 569—620).—The authors discuss equilibria in ternary systems with a miscibility gap in the solid state. The paper does not lend itself to abstraction, but the main results arrived at are briefly as follows.

Where a gap of miscibility occurs in which is exhibited only one solid triangle, and if the gap is maintained throughout the crystallisation, it always gives origin to a point of invariant equilibrium. This point may be of three kinds: (a) A eutectic point, in which case a liquid may deposit the three solid phases. In this point meet the three curves of univariant equilibrium, which all fall towards it. The eutectic point is always found within the solid triangle. (b) A transition point of the first order, and then a liquid may react with a solid phase, previously separated, to give rise to two other solid phases. Two curves of univariant equilibrium fall towards this point and meet in it, whilst a third, also of univariant equilibrium, falls away from it. (c) A transition point of the second order, a liquid then reacting with the two phases previously deposited, giving rise to the third solid phase. Only one curve of univariant equilibrium falls towards this point and two away from it.

The curves of univariant equilibrium, in their turn, may give rise to the three following cases: (a) the curve falls continuously from one end to the other, in which case it can either arrive at or start from the invariant point; (b) the curve presents a minimum of temperature, one of its ends then starting from the invariant point; (c) the curve exhibits a temperature maximum, when it reaches the invariant point at one end. The authors treat only of the first of these three cases.

Where, instead of one gap, there are two distinct ones, the above considerations apply to each separately. Where the two gaps touch, there results a single more complex gap; this case is also discussed.

T. H. P.

Phenomena of Crystallisation in Ternary Systems. IV. Certain Cases of Solubility Gaps. NICOLA PARRAVANO and G. SIKOVICH (*Gazzetta*, 1911, 41, i, 621—644. Compare preceding abstract).—Of the innumerable cases of solubility gaps in ternary systems, the authors discuss the following ten:

(1) The miscibility gap concerns only one binary system; (2) two binary systems exhibit miscibility gaps, whilst the third forms a continuous series of mixed crystals; (3) all three component binary systems exhibit miscibility gaps; (4) one of the binary systems does not form mixed crystals, each of the other two giving continuous series; (5) two of the binary systems do not form mixed crystals, while the third gives a continuous series; (6) two of the binary systems do not give mixed crystals, the third exhibiting a miscibility gap; (7) none of the three binary systems forms mixed crystals; (8) two of the binary systems form no mixed crystals, the third showing two miscibility gaps; (9) four solid phases are formed, the three components and a binary compound; (10) no mixed crystals are formed, but a ternary compound.

T. H. P.

Criterion of the Formation of a Compound in the Condensation of Two Gases. E. BRINER (*Zeitsch. physikal. Chem.*, 1911, 77, 245—249).—An answer to the criticisms of Scheffer (this vol., ii, 379). The main point at issue is the bearing of dissociation on the proof of the formation of a compound between two gases on condensation. The author considers that when condensation takes place at the same composition at different temperatures a compound which is only very slightly dissociated is formed, but when the compound is highly dissociated the process of liquefaction may closely resemble that of mixture of two gases which do not combine chemically.

G. S.

Equilibrium in the System: Lead Nitrate and Pyridine. JAMES H. WALTON, jun., and ROY C. JUDD (*J. Amer. Chem. Soc.*, 1911, 33, 1036—1041).—The solubility of lead nitrate in pyridine has been determined at various temperatures between  $-19.4^{\circ}$  and  $110^{\circ}$ . The proportion of lead in the solution and solid phases was estimated by adding to ammonium acetate solution, boiling until the pyridine had been removed, and then titrating with a standard solution of ammonium molybdate, using tannic acid as an indicator. The solubility data show that three compounds are formed within the above range of temperature. Up to  $51^{\circ}$ ,  $\text{Pb}(\text{NO}_3)_2 \cdot 4\text{C}_5\text{H}_5\text{N}$  is the stable solid phase, but this is then converted into  $\text{Pb}(\text{NO}_3)_2 \cdot 3\text{C}_5\text{H}_5\text{N}$ , and at  $96^{\circ}$  the latter is transformed into  $3\text{Pb}(\text{NO}_3)_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ .

H. M. D.

Law of Moduli in the Variation of the Coefficient of Distribution. NICOLAS DE KOLOSOSOVSKY (*Bull. Soc. chim. Belg.*, 1911, 25, 234—238).—It is shown by experiments on the distribution of acetic acid between ether and aqueous salt solutions that in not too concentrated solution each ion acts independently as regards its effect in altering the distribution of the acid; in other words, the law of moduli is followed. The coefficients of lowering for a number of ions, positive and negative, are given in the paper.

G. S.



**Influence of the Masses of the Reacting Substances on the Formation of Oxonium Dibromides in Different Organic Solvents.** WLADIMIR W. TSCHELINZEFF and W. K. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 620—632).—The authors have studied the effect of increasing the proportion of the ether on the formation of oxonium dibromides in the eight solvents employed in their previous experiments (this vol., i, 256).

The results show that in the majority of cases, increase of the amount of ether is accompanied by only a slight increase in the amount of oxonium compound formed. If two mols. instead of one of ether are used to one mol. of bromine, an appreciable increase in the heat effect is observed, and the increases in the amount of oxonium dibromide formed are, in general, inversely as the amounts formed by equimolecular proportions of the reacting compounds. Corresponding changes are produced by using 3—5 mols. of ether. On the basis of the amount of dibromide formed from 5 mols. of ether and one molecule of bromine, ethyl bromide and benzene change places in the series of solvents given (*loc. cit.*).

T. H. P.

**Influence of the Concentration of the Reacting Substances on the Formation of Oxonium Dibromides in Different Organic Solvents.** WLADIMIR W. TSCHELINZEFF and W. K. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 633—650. Compare preceding abstract).—The following table shows the effect of varying the concentrations of ether and bromine on the percentage yield of oxonium dibromide obtained in different solvents :

Solvent.	Yields of dibromide formed when the reacting substances have the concentrations :			Ratios of the yields.
	2.5N.	1.5N.	0.9N.	
CS <sub>2</sub> .....	15.3	10.4	6.4	2.7 : 1.6 : 1
CCl <sub>4</sub> .....	26.7	15.5	10.1	2.6 : 1.5 : 1
C <sub>2</sub> H <sub>5</sub> Br .....	54.2	6.1	4.6	11.8 : 1.3 : 1
Light petroleum ...	63.3	43.4	14.5	4.4 : 3.0 : 1
C <sub>2</sub> H <sub>5</sub> Br <sub>2</sub> .....	67.9	3.7	1.2	56.6 : 3.1 : 1
CHCl <sub>3</sub> .....	68.0	38.6	17.7	3.8 : 2.2 : 1
C <sub>6</sub> H <sub>6</sub> .....	69.6	10.5	5.6	12.4 : 1.9 : 1
C <sub>6</sub> H <sub>5</sub> Br .....	82.3	40.8	10.8	7.6 : 3.8 : 1

Only with carbon disulphide and carbon tetrachloride does the yield increase proportionately to the concentration of the reacting substances. The results show clearly that, with change of concentration, the arrangement of solvents in the order of their retarding influences on a chemical reaction also changes essentially ; further, that the special influence of the solvents does not vanish with ever increasing dilution.

Further experiments with the various solvents show that there exist three regions of concentration of the reacting substances, distinguished by the following relations : in the first, the region of low concentrations, the reaction is retarded so much that it is only sensible in the first few moments, and, although it begins, it comes almost immediately under the influence of the medium, which opposes the chemical affinity ; in the second region, the strength of the chemical forces begins to overcome the retarding influence of the solvent, in

consequence of which the process proceeds further, although still slowly; finally, in the third region of concentration, the chemical forces preponderate to such an extent that the retarding action of the solvent only begins to be felt near the end of the reaction, when the concentration of the reacting substances diminishes. T. II. P.

**Application of the Phase Rule in Stereochemistry and the Recognition of Racemic Compounds.** ALBERT LADENBURG (*Ber.*, 1911, 44, 1677. Compare this vol., ii, 265; Van der Linde, this vol., ii, 477; Kruyt, *ibid.*).—The author maintains that his method for the recognition of racemic compounds is applicable to liquid racemates.

F. B.

**Hydrolysis of Metallic Alkyl Sulphates.** W. A. DRUSHEL and G. A. LINHART (*Amer. J. Sci.*, 1911, [iv], 32, 51–60).—Kremann (*Abstr.*, 1910, ii, 596) has found that the hydrolysis of barium ethyl sulphate is retarded by the addition of dilute ( $N/2$ ) hydrochloric acid, and was unable to find a velocity constant to represent the behaviour of the reaction. The authors find, on the contrary, that the hydrolysis of the ester is accelerated by hydrochloric acid in all dilutions. Both ethyl hydrogen sulphate and the barium salt are hydrolysed extremely slowly by water even at 60°.

When hydrochloric acid is added to a solution of barium ethyl sulphate, double decomposition takes place with formation of a certain amount of ethyl hydrogen sulphate. On the assumption that the two esters (the acid and the barium salt) are of equal stability, and that the rate of hydrolysis is proportional to the total acid and ester concentrations, a comparatively simple formula is derived which represents satisfactorily the course of the reaction, especially when allowance is made for the different degrees of ionisation of the reacting substances.

In strong aqueous hydrochloric acid ( $2-4N$ ), the formation of barium sulphate is probably chiefly due to the hydrolysis of the ethyl sulphuric acid (equation below) to sulphuric acid, and its subsequent combination with the barium chloride liberated from the barium ethyl sulphate by double decomposition:  $Ba(SO_4Et)_2 + 2HCl \rightleftharpoons BaCl_2 + 2HSO_4Et$ . G. S.

**Influence of Neutral Salts on the Velocity of Reaction.** G. POMA (*Gazzetta*, 1911, 41, i, 353–383).—After a theoretical summary of this question, the author describes his own experiments on the influence exerted on the hydrolysis of ethyl acetate by hydrochloric, hydrobromic, hydriodic, and nitric acids by varying proportions of potassium, sodium, lithium, barium, strontium, and magnesium salts having similar anions to the acids. The experiments were carried out at 20°.

The results show that all the chlorides used cause the catalytic power of the hydrogen ions to increase to approximately the same extent, the differences nearly coinciding with the limits of experimental error. Using the method indicated by Kay (*Abstr.*, 1900, ii, 198) to calculate the diminution in the dissociation of hydrochloric

acid produced by the presence of chlorides, it appears that the percentage increase of the reaction constant increases with the concentration and more rapidly than it. Indeed, the increases divided by the ionic concentrations tend to constancy and to non-dependency on the dilution. The increment of the reaction velocity is greater for salts of the bivalent than for those of the univalent metals, and, among the latter, it increases with diminution of the atomic weight of the alkali metal. Similar results are given by bromides in presence of hydrobromic acid.

The combined results of the whole series of measurements show that the influence of neutral salts on the velocity of reaction depends in high degree on the nature of their anions, the influence of the cations either being non-existent or else coming within the limits of experimental error. The salts examined have the following order of diminishing influence: chlorides, bromides, nitrates, iodides.

These results are in opposition to the view that the influence of neutral salts on the process of hydrolysis is to be referred to an actual concentration of the solution, owing to the formation of solvates. This action exhibits no apparent parallelism with the electro-affinity of the ions into which the neutral salts dissociate, and hence none with their tendency to form complex compounds.

Salts like potassium chloride which do not form solid hydrates, even at low temperatures, exhibit the maximum accelerating effect on the velocity of reaction, whilst those which, like barium bromide, strontium nitrate, etc., crystallise with various amounts of water, show the least influence.

The marked differences in the intensities of the accelerating action exerted by salts similar in constitution and properties tend to exclude a purely physical explanation.

The explanation advanced by Arrhenius that there exists in solution a chemical equilibrium between the active and inactive forms of the substratum, an equilibrium which may be displaced by variations of temperature and ionic concentration, thus remains probably accurate.

T. H. P.

The Development of the Atomic Theory. IV. Dalton's Physical Atomic Theory. V. Dalton's Chemical Theory. VI. The Reception Accorded to the Theory Advocated by Dalton. ANDREW NORMAN MELDRUM (*Mem. Manchester Phil. Soc.*, 1911, 55, No. 5, 1—22; No. 6, 1—18; No. 19, 1—10. Compare this vol., ii, 267).—Historical.  
T. S. P.

Tabular Grouping of the Elements on the Basis of the Periodic System. EDUARD VON STACKELBERG (*Zeitsch. physikal. Chem.*, 1911, 77, 75—81).—An arrangement of the elements is described, which, when represented on a plane surface, differs from Mendeleeff's arrangement mainly in that each long period occupies one line and the elements of the two short periods are so placed that the first four come on the extreme left above the first four elements of the long periods, the last four on the extreme right above the last four elements of the long periods, so that blanks are left in the middle of the short periods.

Hydrogen is put in the same vertical row as the alkali metals. The advantages of this method of arrangement are discussed. G. S.

Mendeléeff's "Cubic" Periodic System of the Elements and the Arrangement of the Radio-elements in this System. A. VAN DEN BROEK (*Physikal. Zeitsch.*, 1911, 12, 490—497).—A "cubic" system suggested by Mendeléeff when only 58 elements were known, is advocated in place of the present "plane" system to embrace the many new series of elements now known in consequence of the discovery of the rare-gases, the recent investigations of the rare-earths, and the disintegration of the radio-elements. The elements are arranged in ascending order of atomic weight in 8 vertical columns, each with 3 vertical lines of elements and 5 horizontal columns, each with 3 horizontal lines of elements. Beginning with horizontal row *A*1, the 8 elements (He—F) occupy the left-hand sub-columns of the 8 vertical columns; in the next horizontal row *A*2 the 8 elements (Ne—Cl) occupy the middle sub-columns; in the next horizontal row *A*3 the next 8 elements (A—Mn) occupy the right-hand sub-columns. At the 25th element (Fe), horizontal column *B*1 commences, the elements being in the left-hand vertical sub-column, and so on for, in all, 120 possible elements. With this arrangement Na, Cu, Ag, and Au, do not appear in the same vertical row, and the differences between the short and long periods of the old system disappear. The "theoretical" atomic weight of the 120 possible elements (excluding hydrogen) are multiples of two up to 240. The sum of all the differences between the actual and "theoretical" atomic weights of all the known elements is very nearly zero. All the  $\alpha$ -ray producing radio-elements known and the new rare-earths can be accommodated. On the old system there are 38 elements for 18 places between *W* and *U*; on the new, counting only the  $\alpha$ -ray producing disintegration products among the radio-elements, there are 24 elements for 24 places. The Lothar Meyer curves of atomic volume and melting points are simpler on the cubic system than on the old system. F. S.

Radioactivity as a General Property of Matter. THEODOR WULF (*Physikal. Zeitsch.*, 1911, 12, 497—500).—A great number of the known atomic weights are separated by 4 units, the mass of the  $\alpha$ -particle. If the known atomic weights are divided by 4 and arranged in columns from 0 to 9 according to the value of the decimal, of the first 25 elements, 11 have the decimal 0, 9 have the decimal 7, the remaining 5 having other values for the decimal. Of the remaining 57 elements, 9 have the decimal 0 and 11 the decimal 7, the remaining 37 elements being distributed over the other values. Of the whole elements, 20 have the decimal 0 and 20 the decimal 7. This suggests that the atomic weights are made up of two series,  $4n$  and  $4n - 1$ . Similar generalisations have been made by Rydberg (1886) before the discovery of radioactivity, who pointed out that the elements with even valency fall in the  $4n$  series and those with odd valency in the  $4n - 1$  series. These relations suggest that the whole elementary system results by disintegration from the heaviest elements, the helium atom being the fundamental unit. F. S.

**Observations not in Good Agreement with the Existence of Atoms and Molecules.** GAETANO MAGNANINI (*Gazzetta*, 1911, 41, 1, 383—384).—The author has already pointed out (*Annuario Univ. Modena*, 1899–1900, 48) that, not only the consequences of thermodynamics (principle of mobile equilibrium), but, what is more important, chemical phenomena at high temperatures, do not readily accord with the fundamental conception of the atomic and molecular structure of matter.

The chemical association occurring in endothermic reactions: e.g., the formation of ozone from oxygen, of hydrogen peroxide from hydrogen, of oxides of nitrogen from their elements, etc., would not only be unforeseen, but would not be easily explained if, starting from thermodynamical results, they were regarded purely from the point of view of the theory of heat—from the ideas concerning the effects of variation of temperature on the movements of the atomic or molecular particles. It seems probable that the principal reason of the universal acceptance of the atomic and molecular hypothesis lies in its simplicity.

T. H. P.

**Van't Hoff's Hypothesis and the Dissolved Molecule.** ALBERT COLSON (*Bull. Soc. chim.*, 1911, [iv], 9, 576—583).—To explain peculiarities in the behaviour of certain salts the author suggests that the dissolved particle is generally an aggregate of chemical molecules in accordance with Raoult's law, but independent of the degree of dissociation as measured by conductivity. This suggestion is in harmony with Cabour's rule.

The chief facts cited in favour of this view are as follows: The lowering of freezing point produced by quantities represented by the formulæ  $H_2SO_4$ ,  $(ZnSO_4)_2$ ,  $Cr_2(SO_4)_3$  and  $Cr_2O(SO_4)_2$  is the same, and in its amount does not depend on the conductivity of the solutions. It has been shown already (Abstr., 1908, ii, 45) that chromium sulphates in solution show conductivities independent of their state of ionisation, since the violet sulphate, which is the most ionised, in solution shows the lowest conductivity. Zinc chloride in solution always gives results indicating the presence of molecules more complex than  $ZnCl_2$ . Ferric chloride and certain of the trioses and tetroses give depressions corresponding to molecular weights which are too low.

It is pointed out finally that Mathias' theory of the constitution of liquids show that Raoult's law does not imply identity of molecular particles for gases and liquids, but merely that there should be a certain constancy in the association which gives rise to liquid molecules. Conductivity appears to be a characteristic of particles which, disintegrated by dissociation, hydrolysis or double decomposition, revert to the molecular state.

T. A. H.

**Relation of Temperature and Molecular Attraction.** JAMES E. MILLS (*Phil. Mag.*, 1911, [vi], 21, 84—113).—Kleeman's views (Abstr., 1910, ii, 492) in regard to the nature of molecular attraction are criticised and shown to be at variance with the relationship  $\lambda/\sqrt{d} - \sqrt{D} = \text{constant}$ , where  $\lambda$  is the internal heat of vaporisation,  $d$  and  $D$  the densities of the liquid and saturated vapour respectively

at the temperature of vaporisation. For a large number of substances, data are recorded which show that  $\lambda/\sqrt[3]{d} - \sqrt[3]{D}$  is nearly independent of the temperature. A further table of data is given to show that Dieterici's relationship  $\lambda = CRT \ln d/D$  is in remarkably good agreement with experiment at higher temperatures, but that deviations occur at very low vapour pressures.

The third part of the paper is devoted to a theoretical discussion of the relationship between temperature and molecular attraction. The chief result of this is to justify the author's previous conclusion that change of temperature does not change the nature or the magnitude of the force of molecular attraction. The temperature merely determines the orbit that the molecules will follow in obedience to the attractive force.

H. M. D.

**Molecular Attraction. IX. Molecular Attraction and the Law of Gravitation.** JAMES E. MILLS (*J. Physical Chem.*, 1911, 15, 417—462. Compare Abstr., 1909, ii, 862).—The author's equation connecting internal latent heat with molecular attraction was found to hold with twenty-five non-associated substances. It follows from this equation that the individual forces acting between the molecules as they expand from distance  $S_1$  to distance  $S_2$  apart vary as  $\mu M/S^2$ , where  $M$  is the mass of substance considered, and  $\mu$  is a constant. If the total force exerted by one molecule on its neighbours is considered, this is equal to  $f = \mu m/S^2$ , where  $m$  is the molecular weight and  $S$  the average distance apart of the molecules.

The equation developed by Helmholtz, giving the amount of energy liberated by the contraction of the sun under Newtonian gravitation, can be applied to the contraction of a sphere of saturated vapour to a liquid, and by use of a suitable constant the latent heat can be calculated on the assumption that molecular force like gravitation varies inversely as the square of the distance apart of the molecules.

It is suggested that molecular and gravitational force are identical in nature. The ether in the neighbourhood of the molecule is in a state of stress, the intensity of which is  $f = \mu m/S^2$ . The author considers that all the usual definitions of mass assume that Newton's law holds. If mass is defined as the attraction exerted by matter instead of the quantity of matter, Newton's law becomes identical with the above law of molecular force; that is, the total gravitational force of a particle with respect to the rest of the universe is a definite quantity depending only on the specific reaction between that particle and the ether.

R. J. C.

**The Electron Conception of Valence. II. The Organic Acids.** K. GEORGE FALK (*J. Amer. Chem. Soc.*, 1911, 33, 1140—1152. Compare Falk and Nelson, this vol., ii, 101).—A theoretical paper, in which the author suggests a classification of organic acids according to the direction of the valences (as determined by the seat of the negative corpuscles) by which the  $\alpha$ -carbon atom is combined with the other atoms or groups in the molecule. Three classes are thus obtained in which the valence directions are represented respectively by  $\equiv \text{C} \cdot \text{CO}_2\text{H}$ ,  $\equiv \text{C} \cdot \text{CO}_2\text{H}$ , and  $\equiv \text{C} \cdot \text{CO}_2\text{H}$ . The ionisation constants

of the first group are less than 0.01, those of the second range from 0.1 to 0.4, and those of the third are greater than 2. In certain cases substituents may exert constitutive effects which give rise to intermediate values of the ionisation constants.

The ionisation constants of unsaturated acids are also supposed to be determined by the additive action of the valence directions, and these effects are discussed in detail.

H. M. D.

**Polarity of Elements and Radicles Measured in Terms of a Logarithmic Function of the Ionisation Constant.** C. G. DERICK (*J. Amer. Chem. Soc.*, 1911, 33, 1152—1162).—An element or radicle is said to possess positive or negative polarity according to whether it increases the hydroxyl or the hydrogen ion concentration when it is substituted for one of the atoms of hydrogen in water. In other words, a positive radicle increases the affinity constant  $K_a$ , whilst a negative radicle increases the constant  $K_b$  for water. Since the free energy change ( $A$ ) and the affinity constant ( $K$ ) are connected by the equation  $A = RT \ln K$ , it follows that the free energy of ionisation is a logarithmic function of  $K$ . For nearly all organic compounds,  $RT \ln K$  is negative, and the greater the positivity or negativity of a substituting radicle, the greater will be the ionisation. Radicles of greatest polarity will therefore have the smallest values for the free energy of ionisation. On this account, the author suggests the expression  $-1000/\log K$  as a convenient measure of the polarity. Polarity values, expressed in this way, have been calculated for a large number of organic radicles, and these numbers are tabulated alongside the values of  $K$ .

H. M. D.

**Application of Polarity Measured in Terms of a Logarithmic Function of the Ionisation Constant. I. The Use of Polarity in the Explanation of the Reactions of Aldehydes and Ketones.** C. G. DERICK (*J. Amer. Chem. Soc.*, 1911, 33, 1162—1167. Compare preceding abstract).—The mechanism of the spontaneous dehydration of the dihydroxy-forms of aldehydes and ketones is discussed in terms of the author's conception of polarity. If the substitution of negative radicles for hydrogen in neutral aldehydes or ketones decreases the hydroxyl ion concentration to the value for pure water, the dihydroxy-form should be completely stable; in other circumstances the aldehyde or ketone must exist for the most part in the inactive dehydrated condition. It is shown that the carboxyl group is probably more negative than chlorine, and on this account the substitution of the carboxyl group for hydrogen in neutral aldehydes and ketones should make the dihydroxy-form stable at the ordinary temperature. Glyoxalic and mesoxalic acids are referred to as substances in which this influence is operative.

The formation of oximes, hydrazones, and semicarbazones is also examined by reference to the conception of polarity. By taking ammonia as unity, the following polarity values have been calculated: ethylamine 1.452, methylamine 1.433, hydroxylamine <1, semicarbazine 0.447, phenylhydrazine 0.592, hydrazine 0.855. For mole-

cules which are less positive than ammonia, the formation of additive compounds is followed by dehydration, whilst molecules which are more positive than ammonia yield stable hydroxy-additive compounds.

H. M. D.

**Application of Polarity Measured in Terms of a Logarithmic Function of the Ionisation Constant. II. Scale of Combined Influence of Substitution in Organic Compounds.** C. G. DERICK (*J. Amer. Chem. Soc.*, 1911, 33, 1167—1181. Compare preceding abstracts).—In this paper the author criticises the views of Michael (Abstr., 1900, i, 321; 1906, i, 550, 781; 1907, i, 170) and Flurschheim (Trans., 1909, 95, 718) relative to the nature of intramolecular action, and maintains the suitability of the so-called polarity values as a measure of the combined direct and indirect influences of substituting radicles on a given atom in the molecule. The relative influence of a substituting atom or group on the ionisation of an acid is obtained by taking the ratio of the polarity values ( $-1000/\log k$ ) of the substituted and unsubstituted acids and subtracting from this the combined influence of the other atoms in the molecule which is equal to unity.

This combined relative influence has been calculated for a large number of substituted organic acids and the values are tabulated. For the  $\beta$ -,  $\gamma$ -, and  $\delta$ -substituted normal fatty acids, the values representing the influence of various substituents are as follows: chlorine, 0.187, 0.063, 0.023; bromine, 0.210, 0.047, 0.017; iodine, 0.167, 0.033, 0.008; hydroxyl, 0.073, 0.018, —; carboxyl, 0.160, 0.111, 0.083. In no case is the influence less in the  $\beta$ -position than in either the  $\gamma$ - or  $\delta$ -positions. This result is not in agreement with the conclusions drawn by Michael.

H. M. D.

**Application of Polarity Measured in Terms of a Logarithmic Function of the Ionisation Constant. III. Correlation of Chemical Structure with Ionisation.** C. G. DERICK (*J. Amer. Chem. Soc.*, 1911, 33, 1181—1189. Compare preceding abstracts).—It is shown that a general relationship exists between the numbers which are supposed to represent the influence of substitution on the ionisation of organic acids. The "place factors" for chlorine when substituted for hydrogen in normal fatty acids in the  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -positions are respectively 0.6825, 0.1873, 0.0627, and 0.0229. These numbers are approximately in the ratio:  $1 : 1/3 : 1/3^2 : 1/3^3$ . This relationship between the "place factors" is found to hold equally well when hydrogen is replaced by bromine, iodine, hydroxyl, or phenyl. It is not exhibited by acids which contain two carboxyl groups, and for these the deviations increase as the distance between the two carboxyl groups increases. This seems to indicate that both carboxyl groups undergo ionisation.

By means of the above rule of thirds it is possible to calculate the ionisation constants of substituted fatty acids if the  $\alpha$ -"place factor" for the given substituent is known. Examples are given to show the degree of accuracy with which this may be carried out.

When two or more hydrogen atoms of a fatty acid are substituted



by negative atoms or groups, the influence on the ionisation can be deduced by adding together the "place factors" for the different substituents. This is the case whether the rule of thirds is obeyed or not.

H. M. D.

**A Self-regulating Gas Burner.** FRITZ HANFLAND (*Chem. Zeit.*, 1911, 73, 669).—A patent burner, now obtainable, is described, by the use of which steam-ovens, sterilisers, etc., may be kept at constant temperature somewhat above 100°, the principle involved being similar to that of an arrangement described by Ulsch (*ibid.*, 1895, 51, 1183). The mercury regulator is built into the base of the burner, which is therefore self-contained.

J. D. K.

**Constant Level Water-Bath.** H. MINIOR (*J. Pharm. Chem.*, 1911, [vii], 3, 585—586).—The adjustable tube in the usual constant level apparatus is replaced by two tubes, one of which, provided with a perpendicular vent, just rotates easily inside the other, which is provided with a helical vent. The inner tube takes the water supply, and, as it is rotated, the position of its perpendicular vent in relation to the helical vent of the outer tube, which communicates by a side arm with the bath, determines the water level. Both tubes are enclosed in a third, which has a side-arm to carry away the excess of water.

T. A. H.

**Arrangement for Collecting the Condensed Water from the Outside of Reflux Condensers.** L. DREDE (*Chem. Zeit.*, 1911, 35, 723).—A glass cup is fitted on to the bottom of the condenser, below the inlet tube for the water. The water condensing on the outside of the condenser collects in the cup and runs off through an outlet tube fused into the bottom thereof.

T. S. P.

**The General Application of the Geryk Air Pump to Vacuum Distillations.** G. DOBY (*Chem. Zeit.*, 1911, 35, 756).—In using the Geryk pump for vacuum distillations, the author inserts absorption flasks containing concentrated sulphuric acid, and calcium chloride and phosphoric oxide tubes, to prevent water and alcohol getting at the pump. This method has the drawback that the sulphuric acid rapidly becomes hot and must be changed very often; to obviate this a reflux condenser, preferably three Soxhlet double surface condensers in series, is inserted between the receiver of the distillation apparatus and the absorption flasks. With this arrangement, 8—10 litres of alcohol can be distilled in eight hours under a pressure of 8—10 mm., and a bath temperature of 40—50°, without the sulphuric acid becoming warm in the least.

T. S. P.

**Safety-valve for Water Pumps.** ARMAND BERG (*Bull. Soc. chim.*, 1911, [iv], 9, 621—623).—The author describes a device for insertion between a water-pump and apparatus under evacuation. The device is designed to (1) prevent entry of water into the apparatus should the water pressure fail and a back-flow occur, and (2) re-

establish action when the water pressure becomes normal. The device is figured, and its mode of action described in detail in the original.

T. A. H.

**A Safety Wash-Bottle** GUSTAV HAPPE (*Chem. Zeit.*, 1911, 35, 656).—The gas delivery tube of the wash-bottle is enlarged considerably in diameter within the bottle so that it is more than capable of taking the whole of the washing liquid, and a safety funnel is also fused in it. Liquid cannot therefore be sucked back into the bottle, nor can the washing liquid rise up into the inlet tube for the gas. The gas delivery tube is open to its full width at the bottom, in order to prevent any stoppage by the formation of crystals, and the bottom of the tube is also made zig-zag, so as to break up the gas bubbles.

T. S. P.

**A Self-acting Wash-Bottle.** JOHANN HAIN (*Chem. Zeit.*, 1911, 35, 697).—The jet-tube of the wash-bottle is elongated to such an extent that when filled with the liquid in the bottle it acts as a siphon.

T. S. P.

**Cutting Tubes by Etching.** JAROSLAW MILBAUER (*Chem. Zeit.*, 1911, 73, 669).—A wet string is tied in a single knot round the (porcelain) tube, supported horizontally on fork rests. One end of the string is placed in a suitable vessel above the tube containing aqueous hydrofluoric acid (preferably mixed with 1/3 vol. of hydrochloric acid), the other in an empty vessel below. As etching proceeds the string is tightened, unevenness being avoided by turning the tube and shifting the knot round. When etched far enough, the tube is wrapped in a cloth and severed by bending.

Quartz tubes may be readily cut in like manner.

J. D. K.

**Preparation of Indigotin as a Laboratory Exercise and as a Lecture Experiment.** FRANZ MICHEL (*Chem. Zeit.*, 1911, 35, 755–756).—Ten parts of phenylglycine-*o*-carboxylic acid, or the corresponding amounts of the sodium or potassium salt, are dissolved in 10–12 parts of a solution of sodium hydroxide (1:4 or 6), and the solution evaporated rapidly to dryness on the water-bath. The powdered residue is then added, stirring well meanwhile, to 8–14 parts of paraffin wax (m. p. ca 60°) heated at 250–270° in a nickel crucible. The reaction is complete when the fusion has become strongly yellow. The cold product may then be extracted with hot water under exclusion of air (or after addition of sodium hyposulphite), or the paraffin may be dissolved away with chloroform, etc. The indoxyl-containing products are then oxidised to indigotin by boiling the aqueous solution in the air, a 90% yield of indigotin being obtained.

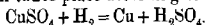
Indirubin may be obtained as follows: the fusion is dissolved in boiling 10% acetic acid, the filtrate from the paraffin made strongly alkaline with ammonia, and the indigotin precipitated by oxidation with a rapid current of air. Extraction with ether then dissolves the indirubin, indigotin remaining undissolved.

For a lecture experiment, 0.5–1 gram of the dry mixture of phenylglycine-*o*-carboxylic acid and sodium hydroxide is heated in a test-tube until water vapour is no longer evolved, and the fusion has become yellow. After cooling, the mass is boiled with 4–5 c.c. water, the test-tube is half-filled with water, and shaken in the air, when indigotin is deposited.

T. S. P.

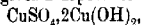
### Inorganic Chemistry.

The Replacement of Metals from Aqueous Solutions of their Salts by Hydrogen at High Temperatures and Pressures. II. WLADIMIR N. IPATIEFF and W. WENKHOWSKY (*Ber.*, 1911, 44, 1755–1758).—Having found previously (*Abstr.*, 1909, ii, 564) that the replacement of metals from aqueous solutions of their salts by hydrogen at high temperatures and pressures is accompanied by the formation of oxides, hydrates, and basic salts, the authors concluded that hydrolysis was a very important factor in the reaction. They now show that the reaction between copper sulphate and hydrogen takes place according to the equation:



The formation of a basic salt and of cuprous oxide is due to secondary reactions.

At 25 atmos. and 90° a *N*/10-solution of copper sulphate, in an atmosphere of hydrogen, gives a deposit of a basic salt,



after ten to fifteen hours. On further heating, cuprous oxide is formed at the expense of the basic salt, which finally disappears. After forty to fifty hours, crystals of copper begin to form, and the cuprous oxide gradually disappears, until after four to seven days only copper remains. Increase of pressure accelerates the above process, diminution in pressure retarding it, as also does rise in temperature. At 90° and under 200 atmos., complete deposition of the copper takes place.

When sufficient sulphuric acid is present, precipitation of a basic salt and of cuprous oxide does not occur as a preliminary to the deposition of copper. The formation of the basic salt is due simply to hydrolysis, and occurs when a normal solution of copper sulphate is heated in the air under ordinary pressure at 100°; the formation of cuprous oxide takes place only in the presence of hydrogen. The final disappearance of basic salt and cuprous oxide in the experiments recorded above is due to their solution in the sulphuric acid liberated by the replacement of the copper by hydrogen.

T. S. P.

Decomposition of Water by Metals. MIROSLAW KERNACK (*Compt. rend.*, 1911, 152, 1668–1670).—It is well known that hydrogen and hydrogen peroxide are produced when finely divided

zinc, magnesium or aluminium are shaken with water. Hydrogen peroxide is not formed, however, when all traces of free oxygen are excluded. The reaction probably follows the course: (1)  $\text{Zn} + \text{H}_2\text{O} = \text{Zn} + \text{OH} + \text{H}$ ; (2)  $\text{Zn} + 2(\text{OH}) = \text{Zn}(\text{OH})_2$ ; (3)  $2\text{H} + \text{O}_2 = \text{H}_2\text{O}_2$ ; (4)  $\text{Zn} + \text{H}_2\text{O}_2 = \text{Zn}(\text{OH})_2$ . When oxygen is absent, reactions (3) and (4) do not occur. The decomposition of water by the electric current and by negative electrons emitted by metals is discussed. W. O. W.

**Formation of Oxidising Agents in Air Under the Influence of Ultra-violet Light.** W. G. CHLOPIN (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 554—561; *Zeitsch. anorg. Chem.*, 1911, 71, 198—205. Compare Kernbaum, Abstr., 1909, ii, 364, 714, 717; Courmont, Nogier, and Rochaix, Abstr., 1909, ii, 723; Berthelot and Gaudechon, Abstr., 1910, i, 349; ii, 564, 606).—The author's experiments show that the ordinary moist air of a room, after subjection for a few minutes to the action of ultra-violet light, shows the presence of ozone, hydrogen peroxide, and nitrogen trioxide. T. H. P.

**Molecular Weights and Constitutional Formulæ of Nitric and Sulphuric Acids.** GIUSEPPE ODDO and GIOVANNI A NELLI (*Gazzetta*, 1911, 41, i, 552—568).—It has been shown (Oddo and Scandola, Abstr., 1910, ii, 1035) that in cryoscopically absolute sulphuric acid (that with the highest freezing point,  $10\cdot43^\circ$ , absolute sulphuric acid not existing in the liquid state), methyl sulphate is partly decomposed to form the acid ester,  $\text{MeH}_3\text{S}_2\text{O}_6$ . The determination of the molecular weight of methyl sulphate in acetic acid or benzene gives results corresponding with  $\text{Me}_2\text{SO}_4$ , and thus excludes the view that the formation of the tri-acid sulphate depends on the existence of a double molecule of methyl sulphate. It hence becomes necessary to assume that sulphuric acid itself has the double formula  $(\text{H}_2\text{SO}_4)_2$ .

In view of the discordant results which have been obtained by different investigators for the molecular weight of sulphuric acid, the authors have made the three following series of measurements.

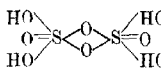
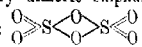
I. The vapour density of cryoscopically absolute sulphuric acid, determined by Victor Meyer's method in anthracene or triphenylmethane vapour, gives the molecular weight  $101\cdot9$  or  $100\cdot9$ . Hence, at  $10$ — $20^\circ$  above the b. p., the vapour of sulphuric acid must represent a mixture of the molecules  $(\text{H}_2\text{SO}_4)_2$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{SO}_3$ , and  $\text{H}_2\text{O}$  in thermal equilibrium, since the acid undoubtedly undergoes dissociation into  $\text{SO}_3$  and  $\text{H}_2\text{O}$  even at the ordinary temperature. This result is confirmed by similar measurements of sulphuric acid containing varying proportions of water, the values obtained for the molecular weight being  $119$ ,  $100\cdot2$ , and  $103\cdot2$ . With acid containing an excess of the trioxide, the vapour tube is attacked, dissociation of the trioxide into dioxide and oxygen taking place.

II. The molecular weight of the purest obtainable nitric acid was determined cryoscopically in nitrobenzene (compare Ampola and Carlinifanti, Abstr., 1897, ii, 12) and in ethylene bromide (compare Raoult, Abstr., Abstr., 1884, 952), which are regarded as associating solvents, but the values obtained were only slightly higher than those

corresponding with the single molecule  $\text{HNO}_3$ . Similar values were obtained in acetic (Baoult, *loc. cit.*) and chloroacetic acids (compare Mameli, Abstr., 1910, ii, 182). With ethylene bromide (compare acid containing a little water (m. p.  $10.52^\circ$ ) causes the separation of an aqueous layer at the surface, but in nitrobenzene its molecular weight corresponds with the molecule  $(\text{H}_2\text{SO}_4)_2$ . In acetic, chloroacetic, and formic acids, sulphuric acid also gives the doubled molecular weight. The conclusion is hence drawn that ordinary sulphuric acid corresponds with ordinary sulphur trioxide, which is dimeric (compare Oddo, Abstr., 1901, ii, 650), and that monosulphuric acid,  $\text{H}_2\text{SO}_4$ , corresponding with the anhydride, m. p.  $14.8^\circ$ , b. p.  $46.2^\circ$ , is not known in the free state. A similar state of affairs exists with the sulphurous compounds, monosulphurous anhydride being known, but not the corresponding acid. An explanation is thus obtained of the considerable interval between the boiling point of sulphuric acid ( $338^\circ$ ) and those of the anhydride ( $46.2^\circ$ ) and sulphuryl chloride ( $69.1^\circ$ ), the differences being much less with the corresponding nitric acid derivatives:  $\text{N}_2\text{O}_5$ ,  $47^\circ$ ;  $\text{NO}_2\text{Cl}$ ,  $5^\circ$ ;  $\text{HNO}_3$ ,  $86^\circ$ .

III. To prepare triacid salts,  $\text{MH}_3(\text{SO}_4)_2$ , it is only necessary to dissolve the normal sulphates or chlorides in the calculated quantity, or rather more, of cryoscopically absolute sulphuric acid and allow the solution to dry on a porous tile in a vacuum over phosphoric anhydride. To prepare the corresponding salts of organic bases, the calculated quantities of cryoscopically absolute sulphuric acid and the base are poured separately into light petroleum; the sulphate immediately separates as an oil, and can be caused to crystallise. A similar result can be obtained by mixing the base and acid directly in the calculated proportions. These compounds will be described later.

Regarding the constitution of ordinary dimeric sulphur trioxide

HO  as represented by:  (compare Oddo, Abstr., 1901, ii, 650), that of ordinary sulphuric acid is best expressed by the annexed formula. A mesohydric formula (compare Oddo, Abstr., 1907, ii, 15) is also suggested.

T. H. P.

#### Action of the Silent Electrical Discharge on Dry and Moist Ammonia. ADOLPHE BESSON (*Compt. rend.*, 1911, 152, 1850—1852).

—When ammonia and hydrogen dried over potassium hydroxide are submitted to the action of the silent electrical discharge, traces of a substance capable of reducing copper sulphate solution are formed. This may be hydrazine, but the amount was insufficient for identification. In presence of water vapour a small quantity of hydroxylamine is formed. A mixture of ammonia and oxygen under like conditions gives no reducing substance, but forms ammonium nitrate and nitrite.

W. O. W.

**Anhydrous Hydrazine. I. A Convenient Apparatus for the Preparation of Anhydrous Hydrazine.** C. F. HALE and FRED F. SHETTERLEY (*J. Amer. Chem. Soc.*, 1911, 33, 1071—1076).—A form of all-glass apparatus is described for carrying out the dehydra-

tion of hydrazine hydrate. It consists of a 500 c.c. flask connected by a ground glass joint with a Vigreux distillation column, which at its upper end is fused to a Liebig's condenser, and this communicates with a graduated cylindrical receiver, which is provided at its lower end with a tap, whilst the upper end is connected with a suitable form of pump. An inlet tube for introducing hydrogen is fused through the walls of the 500 c.c. flask. The results of experiments on the dehydration by means of barium oxide, barium hydroxide, and sodium hydroxide are recorded. According to these, barium oxide appears to give the best results, whilst barium hydroxide is very much less efficient.

H. M. D.

**Aqua Regia.** WILLIAM C. MOORE (*J. Amer. Chem. Soc.*, 1911, 33, 1091—1099).—The behaviour of aqua regia as an oxidising agent is discussed in reference to experiments on the oxidation of mercuric sulphide, lead sulphide, and arsenious sulphide, and of solutions of ferrous ammonium sulphate by nitric acid and by solutions containing hydrogen, nitrate, and chloride ions. The preliminary results show that there are differences in the rates of oxidation which may be due to the influence of excess of hydrogen ions or to a catalytic action of the chloride ion. In the oxidation of ferrous salts the chloride ion appears to act as a negative catalyst.

H. M. D.

**Action of Syrupy Phosphoric Acid on Alloys Prepared by the Electric Furnace.** MAX WUNDER and E. JANNERET (*Compt. rend.*, 1911, 152, 1770—1771).—Certain metals and alloys difficult to attack in the ordinary way are readily dissolved when in a finely divided condition, by heating with phosphoric acid, D 1.75. Silicon after three hours' treatment at 230° gives a colourless liquid, with a gelatinous substance in suspension. Zirconium is dissolved in a few minutes, tungsten less rapidly. Ferrosilicon, ferrotitanium, ferrozirconium, ferrovanadium, silicomanganese, titanium nitride, boron nitride, and ferrosilicon containing aluminium all give clear liquids. Carborundum is entirely decomposed in three hours, giving a syrupy liquid containing a gelatinous precipitate. Carbon in the alloys remains undissolved. Addition of water or acids to the above solutions, produces no precipitate.

W. O. W.

**Compounds of Sulphur and Phosphorus. II. Syntheses with Yellow Phosphorus.** JULIUS MAI (*Ber.*, 1911, 44, 1725—1727. Compare this vol., ii, 484).—Hot solutions of sulphur in aromatic hydrocarbons readily dissolve yellow phosphorus, and at higher temperatures the products of reaction are obtained in the crystalline form.

To prepare  $P_4S_7$ , a cold saturated solution of 3 grams of phosphorus and 5.2 grams of sulphur in carbon disulphide is added to 20 grams of naphthalene heated to 110°; the temperature is gradually raised to 195°. The sulphide crystallises out on cooling, and is purified by extraction of the naphthalene with carbon disulphide, benzene, and light petroleum successively.

The pentasulphide,  $P_4S_{10}$ , is prepared similarly, using 4 grams of phosphorus, 13 grams of sulphur, and 35 grams of naphthalene.

Naphthalene as a solvent can be replaced by xylene, using iodine as a catalyst, but even with excess of sulphur the heptasulphide,  $P_4S_7$ , only is obtained.

Attempts to prepare the trisulphide,  $P_4S_3$ , in the above manner met with no success.

T. S. P.

**Allotropic Modifications of Arsenic and its Melting Point.** PIERRE JOLIBOIS (*Compt. rend.*, 1911, 152, 1767—1769. Compare Güntz and Broniewsky; *Abstr.*, 1907, ii, 948).—From observations by the thermal method the existence of only two allotropic modifications of arsenic is admitted. The ordinary grey variety is stable up to its m. p.,  $850^\circ (\pm 10^\circ)$ . This was determined in a quartz tube by means of a thermocouple. A yellow vapour began to be visible at  $700^\circ$ , and the liquid remained turbid up to  $1100^\circ$ . The unstable form of arsenic prepared by the action of stannous chloride on a solution of arsenious oxide in hydrochloric acid undergoes an irreversible transformation into the grey variety at  $285^\circ$ ; it appears to be identical with the lustrous modification formed when the element is distilled in a vacuum.

W. O. W.

**The Adsorption of Arsenic by Aluminium and Ferric Hydroxide.** GEORG LOCKEMANN and M. PAUCKE (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 273—288).—The results of the experiments with ferric hydroxide have been described previously (this vol., ii, 485). When aluminium hydroxide is precipitated from a solution containing arsenic as arsenite or arsenate, the arsenic is adsorbed by the precipitated hydroxide. The removal of the arsenic takes place more readily at  $80$ — $90^\circ$  than at the ordinary temperature. From solutions which contain less than 20 mg. of arsenic per 100 c.c., the arsenic can be completely removed by the precipitation process, but the quantity of hydroxide requisite for this is very large, the ratio  $Al(OH)_3:As$  increasing from about 15,000 in the more concentrated solutions to about 100,000 in the most dilute solutions investigated. Arsenic is also partly removed by adsorption when solutions of egg-albumin and blood-serum are coagulated. Adsorption effects are further found when arsenic solutions are shaken up with animal charcoal.

H. M. D.

**The Boric Acids.** ALFRED HOLT (*Mem. Manchester Phil. Soc.*, 1911, 55, No. 10, 1—9).—The experiments described in this paper were carried out to see whether the meta- and pyro-acids were really definite compounds or mixtures, and whether any other acids existed.

In the first series of experiments, a weighed amount of orthoboric acid was heated in a platinum dish at constant temperatures of  $98^\circ$ ,  $120^\circ$ , and  $150^\circ$  respectively, and the loss in weight determined from time to time. The second series of experiments consisted in the determination of the melting points of mixtures of orthoboric acid and boric anhydride, intimate mixtures of these two substances being heated in sealed capillary glass tubes. The changes in vapour

pressure on heating orthoboric acid at  $70^{\circ}$  and  $180^{\circ}$  were next examined. Finally, cryoscopic measurements were made on the molecular condition of the boric acids in aqueous solution; three portions of the ortho-acid were heated until one had the composition of metaboric acid, the second of pyroboric acid, and the third was completely dehydrated. Solutions of these portions, as well as the ortho-acid, were then prepared of such strength that each contained the same amount of boric anhydride per c.c. of water.

The results arrived at are as follows: Metaboric acid is probably a definite compound, or hydrate of boric anhydride. No clear evidence can be found for the existence of any acid containing less water than metaboric acid. Only orthoboric acid can exist in solution, under which conditions it is present in simple molecules. Metaboric acid cannot be regarded as an equimolecular mixture of orthoboric acid and boric anhydride. Fused mixtures of orthoboric acid and boric anhydride, in which the molecular ratio of the latter to the former compound exceeds 4:1, can exist in a vitreous metastable and a crystalline form.

Orthoboric acid is readily soluble in hot glacial acetic acid, from which it separates out unchanged on cooling. The pyro-acid and boric anhydride are insoluble, whilst metaboric acid dissolves to a very slight extent, the solution depositing the ortho-acid on cooling.

T. S. P.

**Preparation of Selenium Boride from Iron and Manganese Borides.** J. HOFFMANN (*Chem. Zeit.*, 1911, 35, 713).—When iron boride (ferroboron) is heated in selenium vapour, a porous mass similar in appearance to ferrous sulphide is obtained, which is contaminated by a yellowish-grey product. The latter substance is selenium boride,  $B_2Se_3$ , as shown by its interaction with water. A similar action takes place when iron boride is heated in a current of hydrogen selenide, but the method is not a convenient one, as the temperature required is very near the softening point of hard glass.

Manganese boride reacts with selenium vapour at a red heat, forming a homogeneous yellow to yellowish-green mass, which is a mixture of selenium boride and manganese selenide.

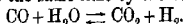
T. S. P.

**Pyrogenic Reactions of Carbon Dioxide with Carbon Disulphide and Hydrogen Sulphide.** RICHARD MEYER and SIEGFRIED SCHUSTER (*Ber.*, 1911, 44, 1931—1944).—In the elementary analysis of organic sulphur compounds, Meyer and Stadler (*Abstr.*, 1884, 1215) found that carbon monoxide was sometimes produced. Its formation was explained by the reduction of carbon dioxide by sulphur dioxide formed during the combustion. The authors in question obtained small quantities of carbon monoxide when they passed a mixture of carbon and sulphur dioxides over glowing copper spirals, but the present authors find that only a trace of carbon monoxide is formed when such a mixture is passed through a red-hot tube, whether the tube is empty or filled with copper. It is possible that carbon disulphide is produced during the combustion of the sulphur compounds, and the authors find that considerable quantities



of carbon monoxide are produced when a mixture of carbon dioxide and disulphide is passed through a red-hot tube, the reaction being  $\text{CO}_2 + \text{CS}_2 \rightleftharpoons 2\text{CO} + \text{S}_2$ ; it is reversible. Possibly also the reaction  $\text{CO} + \text{S} \rightleftharpoons \text{COS}$  takes place.

Other gases, such as hydrogen sulphide and water vapour, might be present in the combustion tube, and the authors find the following reactions to take place at a red-heat:  $\text{CO}_2 + \text{H}_2\text{S} \rightleftharpoons \text{CO} + \text{H}_2\text{O} + \text{S}$ . Hydrogen is formed at the same time by the reaction



The following reactions take place between carbon disulphide vapour and moist carbon dioxide at a red-heat: (1)  $\text{CO}_2 + \text{CS}_2 \rightleftharpoons 2\text{CO} + 3\text{S}_2$ ; (2)  $\text{CO} + \text{S} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2\text{S}$ . Subsidiary reactions are: (3)  $\text{CO} + \text{S} \rightleftharpoons \text{COS}$ , and (4)  $\text{H}_2\text{S} \rightleftharpoons \text{H}_2 + \text{S}$ .

Mixtures of sulphur dioxide and carbon disulphide, both dry and in the presence of water vapour, and moist or dry mixtures of carbon dioxide and sulphur vapour do not give rise to carbon monoxide when heated.

It is, therefore, probable that the formation of carbon monoxide observed by Meyer and Stadler was due to the action of carbon disulphide, or other volatile organic sulphur compound, on carbon dioxide; also, possibly, the reaction between carbon dioxide and hydrogen sulphide may play some part.

T. S. P.

**Carbon Telluride,  $\text{CTe}_2$ .** ALFRED STOCK and HERBERT BLUMENTHAL (*Ber.*, 1911, 44, 1832—1838).—When an arc is formed under carbon disulphide between a tellurium cathode and a graphite anode (compare Abstr., 1905, ii, 315), the tellurium is rapidly vaporised, and condenses, for the most part, in the form of a fine black powder. At the same time the carbon disulphide becomes yellow to brownish-red in colour, and acquires a penetrating, very disagreeable odour. On exposure to daylight, the filtered solution soon, in direct sunlight immediately, deposits a black precipitate. If the yellow solution is concentrated by evaporation on the water-bath, and then heated in a sealed evacuated tube at  $175^\circ$  for forty-eight hours, a greyish-black deposit is obtained, the carbon disulphide not being affected.

Investigation of this greyish-black deposit showed it to consist of carbon and tellurium. It was analysed by heating in a vacuum to sublime the tellurium from the carbon, and weighing the carbon and tellurium separately, the carbon also being burned to dioxide and weighed. The results point to the formula  $\text{CTe}_2$  for the unstable compound dissolved in the carbon disulphide, which is readily decomposed by exposure to light or a high temperature.

On evaporation, the yellow solution in carbon disulphide leaves a viscid, brown residue, which will again dissolve to a yellow solution if immediately treated with the solvent, but otherwise becomes solid and greyish-black in a few seconds, decomposing into carbon and tellurium. The same solution at  $-100^\circ$  gives glistening, brown crystals, which dissolve on slightly raising the temperature.

The solution of carbon telluride has an unbearable penetrating odour, even when so dilute as 0.1%. Smelling a somewhat stronger

solution for only a short time is enough to impart an intense odour of garlic to the breath for several days.

T. S. P.

**Preparation of Colloidal Silicic Acid.** ERICH EBLER and M. FELLNER (*Ber.*, 1911, 44, 1915—1918).—Completely clear and stable colloidal solutions of silicic acid are obtained when silicon tetrachloride vapours, diluted with an indifferent gas, are passed into water through a mercury trap, the water being continuously stirred. A solution obtained by treating 500 c.c. of water with 10—20 grams of silicon tetrachloride could, after dialysis, be concentrated until it contained 9% of silica without gelatinising. The specific conductivity of a solution obtained from 40 grams of silicon tetrachloride and 2000 c.c. of water was  $\chi_{18} = 1.7 \times 10^{-5}$  after dialysing for twenty-two days.

Colloidal solutions of silicic acid obtained by Graham's method from sodium silicate and hydrochloric acid still contain sodium after very prolonged dialysis.

T. S. P.

**Hydrates of Potassium Thiosulphates, their Solubility, and Transition Points.** INOHIKO JO (*Mem. Coll. Sci. Eng. Kyōto*, 1911, 3, 41—49).—The solubility has been determined at 0° and between 17° and 89°, and from the curve obtained the transition points of the hydrates, namely, 35.0°, 56.1°, and 78.3°. The course of the curve indicates another break between 0° and 17°. The composition of the long-known hydrates has also been confirmed by analysis of the residues at intermediate temperatures, namely:  $K_2S_2O_3 \cdot 3H_2O$ ;  $3K_2S_2O_3 \cdot 5H_2O$ ;  $K_2S_2O_3 \cdot H_2O$ ;  $3K_2S_2O_3 \cdot H_2O$ . Above 78.3° the salt is anhydrous.

J. D. K.

**Sodium Potassium Carbonates.** YUKICHI OSAKA (*Mem. Coll. Sci. Eng. Kyōto*, 1911, 3, 55—61).—Two double salts are described in the literature of the subject:  $Na_2CO_3 \cdot K_2CO_3 \cdot 12H_2O$  and  $2Na_2CO_3 \cdot K_2CO_3 \cdot 18H_2O$ .

The author has determined the solubility of the mixed carbonates at 25°, and draws the conclusion that the only double salt that can exist in presence of its solution corresponds with the former. His results agree closely with those obtained at 24.2° by Kremann and Zitek (*Abstr.*, 1909, ii, 572), who, however, give  $6H_2O$ , which the author has traced to an error in calculation.

J. D. K.

**Reaction between Sodium and Mercury.** LOUIS KAHLBERG and DAVID KLEIN (*J. Physical Chem.*, 1911, 15, 471—473).—The liberation of hydrogen when sodium is dissolved in mercury has often been observed, and Lockyer (*Chem. News*, 1879, 40, 101) found it impossible to obtain sodium free from hydrogen even by heating it in a vacuum. The authors find that if clean dry sodium of ordinary quality is dissolved in mercury in absence of water no hydrogen whatever is liberated. No hydrogen could be detected in the sodium in ordinary use.

R. J. C.

**The "De-salting of Sea-Water" According to Aristotle.** EDMUND O. VON LIPPMAHN [and ERNST ERDMANN] (*Chem. Zeit.*, 1911, 35, 629—630).—Erdmann has investigated the percolation of a 3% salt

solution through porous pots and through the so-called Italian pitchers, which are used in the summer for cooling water. In both cases it was found that the water which percolates through the fresh vessels when immersed in the salt solution is salt. When, however, a pitcher was used which had previously been immersed in fresh water for some time and then dried before being immersed in the salt water, in forty-five minutes 50 c.c. of water had percolated through, which was quite sweet, and gave only a very slight opalescence with silver nitrate. The pitcher had retained so much of the fresh water in which it was previously immersed that the hydrostatic pressure caused by immersion in the salt water forced it to percolate into the interior.

The above observations offer an explanation of a statement of Aristotle that when a corked empty vessel is immersed in sea-water, the water which percolates through is fresh. According to the Greek version the vessel used was made of wax ( $\delta\gamma\gamma\epsilon\iota\omicron\nu\ \chi\epsilon\iota\pi\alpha\upsilon\omicron\nu$  = wax vessel; but since wax is completely impervious to water, the author suggests that the rendering should be  $\delta\gamma\gamma\epsilon\iota\omicron\nu\ \chi\epsilon\iota\pi\alpha\upsilon\omicron\nu$  = earthenware vessel).

T. S. P.

**Reciprocal Solubility of Sodium Carbonate and Sodium Hydrogen Carbonate in Water.** EDOUARD HERZEN (*Bull. Soc. chim. Belg.*, 1911, 25, 227—234).—De Paepé (this vol., ii, 489) has deduced from his experimental results on the reciprocal solubility of sodium carbonate and hydrogen carbonate in water that the former dissociates into  $\text{Na}^+$  and  $\text{NaCO}_3^-$  ions, the latter into  $\text{H}^+$  and  $\text{NaCO}_3^-$  ions. The author points out the impossibility of the existence of any appreciable amount of  $\text{H}^+$  ions in alkaline solution, and shows, on the basis of an extension to ternary electrolytes of van't Hoff's treatment of equilibrium in salt solutions, that the results of de Paepé are fully in accord with the usual assumptions that the ions chiefly present in such solutions are  $\text{Na}^+$ ,  $\text{NaCO}_3^-$ ,  $\text{CO}_3^{--}$ , and  $\text{HCO}_3^-$ .

G. S.

**An Allotropic Form of Silver.** DRAGOMIR PALITSCH (*Bull. Acad. roy. Belg.*, 1911, 5, 395—414).—Zinc silver alloys containing 7—10% of silver were prepared, and the zinc extracted at low temperature by means of hydrochloric acid. The silver remains behind in the form of a greyish-white powder, which assumes a metallic appearance when compressed. From measurements of the density, the rate at which it dissolves in mercury, the heat of solution in mercury, and the difference of potential which is set up in contact with a solution of a silver salt, the author draws the conclusion that this form of silver represents an allotropic modification.

H. M. D.

**Nature of the Photo-chlorides of Silver.** KONRAD SICHLING (*Zeitsch. physikal. Chem.*, 1911, 77, 1—57). EMIL BAUR (*ibid.*, 58—65).—See this vol., ii, 680, 681.

**Plastic Calcium Fluoride.** ROBERT COHN (*Zeitsch. angew. Chem.*, 1911, 24, 1209. Compare Atterberg, this vol., ii, 605).—When calcium fluoride is precipitated by the addition of milk of lime or of calcium carbonate to a very dilute aqueous solution of hydrofluoric

acid, it forms a white, deliquescent mass. If this is collected and powdered after drying in the air or by gentle warming, the powder obtained can be rolled into wire after the addition of 20–25% of water, whereas with 30% of water the mixture obtained flows. Calcium fluoride is thus a plastic substance.

T. S. P.

**Isomorphous Mixtures of Anhydrous Calcium, Magnesium, and Iron Carbonates.** W. DIESEL (*Zeitsch. Kryst. Min.*, 1911, 49, 250–277).—Working on the lines suggested by G. Linck for the artificial production of dolomite (this vol., ii, 294), solutions of calcium chloride, magnesium sulphate, magnesium chloride, ammonium sesquicarbonate, and ferrous-ammonium sulphate were mixed together in various proportions and of various strengths, the experiments being performed in an atmosphere of carbon dioxide. The gelatinous precipitates after some hours became crystalline, taking the form of minute spherules with weak negative birefringence. The precipitates, dried and filtered in an atmosphere of carbon dioxide, were analysed, and it was found that whilst calcium and iron carbonates mixed together in all proportions, only little magnesium carbonate (not more than 5%) enters into the composition of the spherules. The filtrates from these precipitates contained no iron, only little calcium, and much magnesium. The size and form of the spherules vary with the amount of iron they contain. Determinations of the sp. gr. show that the calcium carbonate is present in the spherules as vaterite (a spheroidal form of calcium carbonate with D 2.54). Vaterite is more active than aragonite, and aragonite more active than calcite, in precipitating iron from a solution of ferrous sulphate. When a mixed magnesium-calcium carbonate is placed in a ferrous sulphate solution, the magnesium is replaced by iron more quickly than is the calcium.

L. J. S.

**The Ternary System  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ .** A Study of the Constitution of Portland Cement Clinker. EARNEST S. SHEPHERD and GEORGE A. RANKIN (With Optical Study by FRED E. WRIGHT). (*J. Ind. Eng. Chem.*, 1911, 3, 211–227; *Zeitsch. anorg. Chem.*, 1911, 71, 19–64).—The method chiefly used for determining the limits of the various fields in the ternary system was as follows: A small amount of material of the desired composition was placed in a furnace and kept at constant temperature until, on quenching, only one kind of crystal was present, the rest of the solution being cooled to a glass before it had time to crystallise. Temperatures could thus be found where the product was wholly glass or wholly crystalline.

In earlier work with mixtures of pure lime and silica, two compounds, the metasilicate,  $\text{CaO}.\text{SiO}_2$ , and the orthosilicate,  $2\text{CaO}.\text{SiO}_2$ , were definitely established, but no trace of the hitherto generally accepted tricalcium silicate could be found. The latter compound is formed immediately, however, in the ternary system on the addition of alumina to mixtures of appropriate lime-silica concentration, and the authors have been able to prepare it pure, except for a small excess (between 1 and 2%) of orthosilicate or lime or both. It appears to be unstable at its m. p., and so does not form from a melt of this composition. For the same reason, it does not form eutectics.

with the adjacent compounds, calcium orthosilicate and lime. Neither is there any evidence that it takes up calcium orthosilicate or lime in solid solution.

A new and probably unstable form of calcium orthosilicate has been obtained by cooling an old and hydrated sample of the orthosilicate rapidly from  $1425^{\circ}$ ; it yields weakly birefracting and optically positive crystals.

In the ternary system nineteen quintuple points are indicated, and the location of the following five have been fixed:

CaO.....	59.5	58.5	52.8	49.2	48.5
Al <sub>2</sub> O <sub>3</sub> .....	32.5	33.0	40.5	44.0	42.0
SiO <sub>2</sub> .....	8.0	8.5	6.7	6.8	9.5

If solid solutions are formed, they are very limited in extent, and are not sufficient to affect the optical properties either of the silicates, lime, or aluminates.

The diagram indicates that the constitution of slag cement will be seriously affected by relatively small differences of composition in the neighbourhood of the lime joining the compounds calcium orthosilicate and  $2\text{CaO}, \text{Al}_2\text{O}_3, \text{SiO}_2$ .

Ferric oxide appears not to form solid solutions with  $\text{CaO}$ ,  $3\text{CaO}, \text{SiO}_2$ ,  $\text{Ca}_2\text{SiO}_4$ , or  $3\text{CaO}, \text{Al}_2\text{O}_3$ . It appears to react in some way with  $5\text{CaO}, 3\text{Al}_2\text{O}_3$ , but the nature of this reaction has not yet been studied.

Attention is called to the fact that ferric oxide dissociates at about  $1400^{\circ}$  with the formation of  $\text{Fe}_2\text{O}_4$ .

A full description is given of the optical properties of the many compounds which occur in the various binary systems and in the ternary system.

T. S. P.

**Artificial Crystallisation of Barium Sulphate.** HERMON C. COOPER, T. S. FULLER, and A. A. KLEIN (*J. Amer. Chem. Soc.*, 1911, 33, 845—847).—Barium sulphate crystals, 5 mm. long and 1 mm. wide, have been obtained by crystallisation from fused barium chloride and from fused sodium sulphate. They were orthorhombic, had  $n_D$  about 1.648, and agreed in these and other respects with the characters of natural barium sulphate (barite) as recorded by Groth.

Le Chatelier's statement (*Abstr.*, 1897, ii, 135), with reference to the curve representing the m. p.'s of mixtures of sodium sulphate with increasing proportions of barium sulphate, could not be confirmed.

E. G.

**Analysis of Aboriginal Copper Objects from Mexico and Yucatan.** AUGUSTUS H. FISKE (*J. Amer. Chem. Soc.*, 1911, 33, 1115—1116).—Analyses of four small copper bells are recorded which show that the original metal of the three objects from Yucatan must have been nearly pure copper. Traces of iron, silver, gold, and silica were found.

In the case of the bell from Mexico, 19.3% of lead was present.

H. M. D.

**Formation of Double Salts.** HARRY W. FOOTE and PERCY T. WALDEN (*J. Amer. Chem. Soc.*, 1911, 33, 1032—1036).—From experiments in which varying proportions of cupric chloride, potassium

chloride, and ethyl alcohol or acetone were shaken up at 25° until equilibrium was attained and the solution and residue analysed, it is found that the only double salt formed is  $\text{CuCl}_2 \cdot \text{KCl}$ . In both cases the cupric chloride combines with the solvent to form solid phases of the composition  $\text{CuCl}_2 \cdot \text{EtOH}$  and  $\text{CuCl}_2 \cdot \text{C}_2\text{H}_5\text{O}$  respectively. Similar determinations made with cupric chloride, ammonium chloride, and ethyl alcohol indicate the formation of solid  $\text{CuCl}_2 \cdot \text{NH}_4\text{Cl}$  and  $\text{CuCl}_2 \cdot \text{EtOH}$ .

H. M. D.

**Vapour Pressures of Mercuric Chloride, Bromide, and Iodide.** FREDERICK M. G. JOHNSON (*J. Amer. Chem. Soc.*, 1911, 33, 777—781).—The values of the vapour pressures of mercuric chloride, bromide, and iodide which have been recorded previously show considerable disagreement, and determinations have therefore been made by the method employed for measuring the dissociation pressures of the ammonium halides (Abstr., 1908, ii, 157; 1909, ii, 23).

In the case of mercuric chloride, the vapour-pressure curve shows a decided break at 277°, corresponding with the m. p. as found by Jonker (Abstr., 1910, ii, 127). The b. p. is 302.5°/760 mm.

The curve obtained for mercuric bromide shows the m. p. to be 236° and the b. p. 318°/760 mm.

The mercuric iodide curve does not show any decided change in the neighbourhood of the m. p. By extrapolation, the b. p. was found to be about 351°/760 mm.

E. G.

**The Stearate Separation of the Rare Earths.** CHARLES W. STODART and C. W. HILL (*J. Amer. Chem. Soc.*, 1911, 33, 1076—1090).—The fractionation of rare-earth mixtures can be conveniently effected by means of an alcoholic solution of potassium stearate which is added to a neutral solution of the earth nitrates in successive quantities sufficient for the precipitation of a portion of the earths present. To obtain good results, the hot alcoholic stearate solution should be added drop by drop to the cold dilute solution of the earth nitrates, the mixture being agitated by a glass stirrer driven at high speed by means of a small electric motor.

The method is applied to the fractionation of the yttrium earths from monazite, and it is shown that the separation of nearly pure yttrium can be effected by quite a small number of fractionations. As has been already found in the application of other methods, there is a slowing down in the progress of the fractionation at the portion which corresponds with an atomic weight of about 102. When applied to the yttrium earths from gadolinite, the stearate method affords a rapid separation without any pause at the fraction of atomic weight 102.

Experiments are also described which show that the gadolinium earths and the members of the cerium group may be separated by fractional precipitation as stearates.

With a view to separating the rare earths of the yttrium series, these were treated with various organic liquids, but fractionation by this method was found to be impossible.

H. M. D.

**Solubility of Aluminium Hydroxide.** WALTER HERZ (*Zeitsch. Elektrochem.*, 1911, 17, 403—404).—Polemical against Slade (*ibid.*, 261).  
T. E.

**The Crystallisation of White Cast Iron.** CARL BENEDICKS (*Intern. Zeitsch. Metallographie*, 1911, 1, 184—191).—The crystallisation of a eutectic mixture, such as that of white cast iron, takes place in such a way as to form "colonies" of definite orientation, having the external form and appearance of homogeneous crystals. The natural cleavage planes of white iron containing an excess of cementite exhibit forms due to the influence of surface tension.  
C. H. D.

**A Fourth Recalescence in Steel.** JOHN O. ARNOLD (*Intern. Zeitsch. Metallographie*, 1911, 1, 192—203).—A thermal investigation of steels containing varying amounts of carbon, and a comparison with iron free from carbon, show that a development of heat occurs during the cooling of steel between the points  $Ar_3$  and  $Ar_1$ . The maximum development of heat occurs in steels containing about 0.45% C, that is, consisting of equal parts of ferrite and pearlite. It is attributed to constitutional segregation of the solid solution to form microscopically distinct masses, which begins at  $Ar_3$  and is complete at  $Ar_1$ .  
C. H. D.

**The Cementation of Chromium Steels.** FEDERICO GIOLITTI and F. CARNEVALI (*Atti R. Accad. Sci. Torino*, 1911, 46, 558—568).—A chromium steel, containing 2.33% Cr, 0.41% C, 0.15% Si, and 1.02% Mn, is subjected to cementation in the manner employed for nickel steel (this vol., ii, 609). Cementation for five hours in ethylene at 950° and at 1050°, with carbon monoxide at the same temperatures, and with carbon and carbon dioxide in different proportions at 1000° and 1100°, show that the differences in the action of these cementing agents observed in the case of carbon steels (Abstr., 1910, ii, 616) also occur with chromium steel. In general, the presence of chromium tends to give rise to an increase in the maximum concentration of carbon in the cemented zone, as compared with that found in a carbon steel cemented under the same conditions.  
C. H. D.

**Experiments with Glaucodote.** A. BEUTELL (*Centr. Min.*, 1911, 411—415. Compare this vol., ii, 485).—Glaucodote, when heated in a cathode vacuum, yields a distillate containing 1.10% of sulphur and 5.43% of arsenic. When the material is alternately roasted and distilled in a vacuum, the yield is 4.38% of sulphur and 23.37% of arsenic. The effect of the roasting is to produce disulphide, which in the vacuum decomposes into monosulphide and sulphur. Less arsenic is distilled from glaucodote than from mispickel. The constitutional formula deduced from these experiments is  $\text{Fe} \begin{smallmatrix} \text{S} - \text{As} \\ | \\ \text{S} - \text{As} \end{smallmatrix} \text{Co}$ , analogous to that arrived at for mispickel. The material, from Håkansböda, Sweden, used in the experiments gave analysis I; deducting copper with the same

spending amounts of iron and sulphur as copper-pyr s, the results under II are obtained.

	S.	As.	Fe.	Co.	Ni.	Cu.	Total.
I. 20'35	38'80	21'83	16'36	0'46	1'93	99'73	
II. 19'56	41'22	21'39	17'37	0'46	—	100'00	

L. J. S.

**Ferroso-ferric Oxide and Ferrous Oxide.** SIEGFRIED HILPERT and JOHANNES BEYER (*Ber.*, 1911, 44, 1608—1619).—The reduction of ferric oxide at 500° by a mixture of hydrogen and steam shows a sharp break in the velocity of reaction when the composition  $\text{Fe}_3\text{O}_4$  is attained. From this observation, the following method for preparing pure  $\text{Fe}_2\text{O}_3$  has been worked out. Ferric oxide is reduced at 400° in a current of hydrogen which has previously passed through wash-bottles containing water at 30—50°. A reduced copper spiral should be inserted between the ferric oxide and the wash-bottles. If the concentration of the aqueous vapour, which at the temperature of the experiment gives a definite partial pressure of oxygen in the presence of the excess of hydrogen, is diminished, metal is produced and not oxides richer in ferrous oxide. At higher temperatures, however, and with increasing concentration of aqueous vapour, products richer in ferrous oxide are formed. Thus, at 700°, the oxide contained 85%  $\text{FeO}$ , and at 800°, 92%  $\text{FeO}$ , the concentration of the aqueous vapour being 38%. Further increase of temperature to 1100° did not, however, give pure ferrous oxide, the purest containing 1.5%  $\text{Fe}_2\text{O}_3$ .

Endeavours to prepare pure ferrous oxide by oxidation of iron with a mixture of hydrogen and steam were unsuccessful, and the various methods given in the literature for the preparation were found to be unsatisfactory.

Magnetic measurements on the various powdered ferroso-ferric oxides obtained indicate the existence of solid solutions. T. S. P.

**The Oxidation of Ferrous Salts.** CHARLES BASKERVILLE and RESTON STEVENSON (*J. Amer. Chem. Soc.*, 1911, 33, 1104—1106).—When oxygen or air is passed through neutral or acid solutions of ferrous salts at the ordinary temperature, oxidation only takes place to a very small extent. The presence of salts of cobalt, chromium, copper, manganese, molybdenum, nickel, titanium, vanadium, and tungsten has no appreciable effect on the rate of oxidation. Dust particles, glass wool, and pumice stone behave similarly, but in presence of platinised asbestos oxidation occurs readily. At temperatures near the boiling point, the rate of oxidation is much greater in all cases.

In alkaline solution, ferrous iron is oxidised quite readily at the ordinary temperature.

From these observations, the conclusion is drawn that the expulsion of air during the reduction of iron solutions by zinc is unnecessary.

H. M. D.

**Fluorides of Cobalt and Nickel.** N. COSTACHESCU (*Ann. Sci. Univ. Jassy*, 1911, 7, 5—13).—No matter in what way the experimental conditions were varied, the author has not succeeded in



preparing the compounds  $\text{CoF}_2 \cdot 5\text{HF} \cdot 6\text{H}_2\text{O}$  and  $\text{NiF}_2 \cdot 5\text{HF} \cdot 6\text{H}_2\text{O}$ , described by Böhm (Abstr., 1905, ii, 249).

Hexa-aquofluorides of cobalt and nickel do not exist, but the tetra-aquo-salts are readily obtained, the cobalt salt forming two isomerides,  $\alpha$  and  $\beta$ .  $\alpha$ -Cobalt-hexa-aquofluoride,  $(\text{H}_2\text{O})_4\text{CoF}_2$ , is obtained in the form of large, garnet-red, rhombic octahedra by dissolving freshly-prepared cobalt hydroxide in 40% hydrofluoric acid, diluting the resulting solution with an equal volume of the acid, and allowing it to crystallise in a vacuum over strong sulphuric acid. The  $\beta$ -salt is produced when the above solution is precipitated with 96% alcohol; it forms small, rose-coloured crystals, and is isomorphous with the corresponding nickel salt. The  $\beta$ -salt is more soluble in water (the saturated solution at room temperature is 2.3203%, whilst that of the  $\alpha$ -salt is 2.2328%) and hydrofluoric acid than the  $\alpha$ -salt; it also loses water more readily, at  $60^\circ$  losing 37.10%  $\text{H}_2\text{O}$ , whilst the  $\alpha$ -salt loses only 9.35%, and is more reactive than the  $\alpha$ -salt. Both salts give identical solutions in water, as shown by measurement of the electrical conductivity. It is probable that the solids are stereoisomerides, in the  $\alpha$ -form the fluorine atoms being situated at the opposite ends of one of the axes of the octahedron, whilst in the  $\beta$ -form they are at the opposite ends of one of the sides.

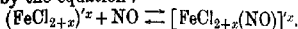
The pyridine derivative,  $[(\text{H}_2\text{O})_2\text{CoPy}_2]\text{F}_2 \cdot \text{H}_2\text{O}$ , is obtained by dissolving either the  $\alpha$ - or  $\beta$ -salt in warm pyridine, filtering the solution, and allowing it to crystallise. It forms brick-red, acicular crystals, which gradually lose pyridine on exposure to the air, leaving the compound  $(\text{H}_2\text{O})_4\text{CoF}_2$ , the extra molecule of water being absorbed from the air. The same compound forms the residue obtained by evaporation of the solutions in alcohol or water.

Nickel hexa-aquofluoride,  $(\text{H}_2\text{O})_6\text{NiF}_2$ , is prepared similarly to the cobalt compound, and forms very pale green crystals. By solution in pyridine, the derivative,  $[(\text{H}_2\text{O})_2\text{NiPy}_2]\text{F}_2 \cdot \text{H}_2\text{O}$ , is obtained in the form of azure-blue crystals, which possess properties similar to those of the corresponding cobalt compound. T. S. P.

**Metal-Nitroso-compounds.** VOLKMAR KOHLSCHÜTTER and P. SAZANOFF (*Ber.*, 1911, 44, 1423—1432).—The authors discuss the results hitherto obtained in the investigation of the absorption of nitrous oxide by solutions of ferrous and ferric salts (compare Abstr., 1910, ii, 956, 1055; this vol., ii, 272); at the same time they contribute some new results with respect to the optical behaviour of such solutions.

The absorption of nitric oxide by a 0.04*N*-solution of a ferrous salt causes the appearance of a broad absorption band in the yellow, extending from 605 to 565  $\mu\mu$ , and corresponding with the reversible reaction:  $\text{Fe}^{++} + \text{NO} \rightleftharpoons \text{Fe}(\text{NO})^{+}$ . If increasing concentrations of hydrochloric, hydrobromic, or sulphuric acid are added to the solution of the ferrous salt, the absorption of nitric oxide increases, although it never exceeds 1 atom of nitric oxide to 1 atom of iron; at the same time the colour of the solution changes, and the absorption band in the yellow gradually disappears. The absorption of nitric oxide is now characterised by the formation of complex anions, which are

more stable than the complex cations mentioned above, as, for example, shown by the equation :



Solutions of ferrous chloride in methyl and ethyl alcohol, acetone, ethyl acetate, etc., containing nitric oxide are optically similar to the solutions in concentrated hydrochloric acid, whereas the solutions in formic acid, pyridine, etc., show the characteristic absorption band of the aqueous solutions. Since ferrous chloride has practically a normal molecular weight in pyridine solution, it follows that simple electrolytic dissociation has practically no effect on the absorption spectrum.

In the case of cupric salts, the optical investigation, which is also confirmed by the direction of migration of the coloured ion, shows that nitric oxide forms part of a complex anion in concentrated aqueous and in alcoholic solutions, and in solutions strongly acidified with hydrochloric or sulphuric acid, whilst in solutions in formic and glacial acetic acid, it forms part of the cation.

The optical investigation affords no support to Raschig's view that in sulphuric acid solutions of copper and iron salts the absorption of nitric oxide is conditioned by the sulphuric acid residue, as in nitrosulphonic acid.

T. S. P.

**Action of Carbon on Chromyl Chloride.** JOSÉ RODRIGUEZ MOURELO and ANTONIO GARCÍA BARRA (*Anal. Fis. Quím.*, 1910, 8, 355—362).—It was thought possible that, on passing carefully dried vapours of chromyl chloride mixed with air over heated carbon, carbonyl chloride would be formed, thus:  $4\text{CrO}_2\text{Cl}_2 + 4\text{C} + \text{O}_2 = 2\text{Cr}_2\text{O}_3 + 4\text{COCl}_2$ . But instead of this action occurring, chromic oxide was formed in the first portion of the tube, and chromic chloride sublimed forward. Difficulty was experienced in obtaining dry wood-carbon free from hydrocarbons, and in the experiments described the carbon used was heated to redness for some time prior to passing the chromyl chloride; even after this treatment, on passing dry chlorine, hydrogen chloride was formed from hydrocarbons retained by the carbon, and a certain amount of sublimate was produced.

On passing a mixture of dry chlorine and chromyl chloride over carbon heated to redness, the proportion of chromic chloride formed is greatly increased at the expense of the chromic oxide, the action  $2\text{CrCl}_2\text{O}_2 + \text{Cl}_2 + 4\text{C} = 2\text{CrCl}_3 + 4\text{CO}$  apparently preponderating. This process affords a simple and rapid means of obtaining well crystallised chromic chloride.

W. A. D.

**Distillation of Tin in a Vacuum.** ERICH TIEDE and FRANZ FISCHER (*Ber.*, 1911, 44, 1711—1717. Compare Schuller, *Abstr.*, 1904, ii, 109; Moissan, *Abstr.*, 1906, ii, 92; Greenwood, *Abstr.*, 1910, ii, 390).—A quantitative separation of lead from tin in an alloy of these two metals was carried out by vacuum distillation in a quartz tube heated in a Heraeus furnace, the vacuum being obtained by an ordinary mercury pump. No trace of tin was carried over by the lead. Even when the temperature of the furnace was raised considerably above that necessary for the distillation of lead, tin could

not be distilled, since air diffused through the quartz and spoiled the vacuum. The authors therefore designed an apparatus, the essential parts of which were as follows. The electric oven proper consisted of a porcelain or magnesia tube, wound round with platinum wire and properly insulated. It was contained in a jacketed glass tube, a stream of cold water flowing continuously through the jacket; the glass tube was connected with a Gaede pump and a tube cooled in liquid air for condensing mercury vapour, all connexions being made of glass with mercury seals. A cathode-light vacuum was maintained during the distillation, the porcelain tube being heated to a bright red heat. The metal to be distilled was placed in a boat in the porcelain tube.

Tin was readily distilled in the above apparatus, collecting on the ends of the porcelain tube. At the same time, with all the purest samples of commercial tin used, a deposit formed on the cold walls of the glass tube, which was at first brass-yellow in colour, finally becoming dark brown to black; it proved to be tin sulphide. Pure tin, prepared from Kahlbaum's stannic chloride, did not give this deposit; a short exposure to the atmosphere of the laboratory was sufficient, however, for some tin sulphide to be formed, as proved by a further distillation.

T. S. P.

**Preparation of Colloidal Vanadic Acid by a New Dispersion Method.** ERICH MÜLLER (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 302—303).—A colloidal solution of vanadic acid is obtained when the molten acid is poured into distilled water. If the solution is evaporated to dryness on the water-bath, the residue obtained is insoluble in water, but is much more reactive than the ordinary form of the acid. It is supposed that the production of the colloidal acid in the above manner is due to the rapidity with which the transition from the liquid to the solid state is effected.

H. M. D.

**Sodium-Gold Alloys.** C. H. MATHEWSON (*Intern. Zeitsch. Metallographie*, 1911, 1, 81—88).—Gold dissolves readily in sodium at low temperatures. The freezing point of sodium is lowered until a eutectic point is reached at 3.6 atomic % of gold and 81°; the freezing-point curve then rises to a maximum at 98.9°, corresponding with the compound  $\text{Au}_2\text{Na}$ , from which it falls to a second eutectic point at 83 atomic % Au and 876°. Solid solutions are not formed to any appreciable extent in any part of the series. The compound  $\text{Au}_2\text{Na}$  is stable in air, but is attacked by hot water, or more rapidly by acids.

Gold may be separated from its alloys with silver by dissolving in molten sodium and subsequently extracting with nitric acid. The residue contains a trace of silver. The alloys of gold and sodium are very rapidly attacked by a dilute solution of potassium cyanide containing hydrogen peroxide. Platinum, if present, remains almost completely undissolved.

C. H. D.

## Mineralogical Chemistry.

**The Platiniferous Deposits of the Urals.** LOUIS DUPARC (*Arch. Sci. phys. nat.*, 1911, [iv], 31, 211—230, 322—345, 439—456, 516—533).—A detailed account is given of the geological relations of the platiniferous districts; and petrographical descriptions, with several analyses, are given of the rocks. The platinum occurs mostly in the dunites, less frequently in the pyroxenites, and it is often associated with chromite. Fifteen analyses by H. C. Holtz (published also in *Tech. Min. Mitt.*, 1910 [1911], 29, 498—504) are given of native platinum collected from the stream beds at various localities; the extreme values are:

Pt.	Ir.Os.	Pd.	Cu.	Rh,Ru,Ir.	Fe.
75.37—88.98	0.28—5.41	0.15—0.99	0.03—1.66	2.79—3.96	7.03—16.60

In most of the analyses, however, Pd, Cu, Rh, Ru, Ir are given together, the extreme values being 3.00—8.04. L. J. S.

**Yttrifluorite, a New Mineral from Norway.** THOROLF VOGT (*Centr. Min.*, 1911, 373—377).—The mineral forms a vein some metres in width in a pegmatite vein intersecting granite in northern Norway (exact locality not stated); associated minerals are fluorite (D 3.2006), orthite, gadolinite, fergusonite, euxenite (?), and xenotime. It is translucent to transparent, yellowish or brownish, and has a vitreous to greasy lustre. There is an imperfect octahedral cleavage, and the material is optically isotropic, belonging therefore to the cubic system. Hardness  $4\frac{1}{2}$ , D 3.5572,  $n_{Na}$  1.4572 (of the material analysed); another sample gave D 3.5356,  $n_{Na}$  1.4522. The composition is also variable; one sample gave the following results, agreeing with  $20CaF_2 \cdot 3YF_3$ :

CaO.	Y <sub>2</sub> O <sub>3</sub> , etc.	Ce <sub>2</sub> O <sub>3</sub> , etc.	Alkalis.	F (calcd.)	Loss on ignition.	Total water.
54.89	17.35	1.68	0.15	45.54	0.67	0.22
						101.33

Spectroscopic examination showed the presence of several other rare earths. Although somewhat resembling fluorite in its characters, the mineral is more nearly related to yttrocerite, but differs from this in containing less cerium earths. These minerals are regarded as forming an isomorphous group with the formulæ: fluorite,  $CaF_2$  or  $Ca_2F_6$ ; yttrocerite,  $(Ca_3,Ce_2,Y_2)F_6$ ; yttrifluorite,  $(Ca_3,Y_2)F_6$ . L. J. S.

**Composition of Blende from Picos de Europa.** RAMÓN LLORD Y GAMBOA (*Anal. Fis. Quim.*, 1910, 8, 413—421).—Blende from Picos de Europa examined by the spectrographic method (compare Urbain, *Abstr.*, 1909, ii, 1026) was found to contain indium (traces), gallium (relatively abundant), and germanium (approximately 1 in 1,000,000). Iron was present in very varying proportions in all the blendes from this locality which were examined, and it is probable that the orange and blood-red specimens owe their colour to this element. The colour

is not homogeneously distributed in the crystals, but exists in zones. One nearly colourless specimen contained only 0.066% of ferrous sulphide. The colourless blendes do not contain manganese, but lead could be detected in these. Cadmium is always present. Calcium, potassium, sodium, and lithium can be detected in nearly all specimens spectroscopically; these are probably present as chlorides, and form the inclusions visible under the microscope. By powdering the mineral very finely and extracting with water, the filtered extract shows the presence of chlorine and the metals named. The aqueous extract from 100 grams also contains 0.007 gram of organic matter, which is volatile and has a turpentine-like smell. The powdered blende after extracting with water no longer showed the presence of calcium, potassium, sodium, or lithium when examined spectroscopically, showing that the metals are present exclusively as soluble chlorides. The extracted blende, however, shows the phenomenon of thermoluminescence, which, therefore, is not due to the presence of these impurities.

W. A. D.

**Muthmannite, a New Mineral.** FERRUCCIO ZAMBONINI (*Zeitsch. Kryst. Min.*, 1911, 49, 246—249).—Attention is called to the fact that the published analyses of krennerite fall into two groups: those containing but little silver and with the ditelluride formula  $[\text{Au}(\text{Ag})]\text{Te}_2$ ; and those containing about 20% silver, which have the monotelluride formula  $(\text{Ag}, \text{Au})\text{Te}$ . It is only those of the former group that were made on material of which the crystallographic identity with the orthorhombic krennerite had been determined. Those of the latter group are taken as representing a distinct species, for which the name *muthmannite* is proposed; the following new analysis of this also agrees with the formula  $(\text{Ag}, \text{Au})\text{Te}$ .

Au.	Ag.	Pb.	Fe, Cu.	Te.	Total.
22.90	26.38	2.58	little.	46.44	98.28

The material analysed resembles krennerite in its external appearance; but the imperfect crystals are tabular and often elongated in one direction, parallel to which direction there is a perfect cleavage. The colour is very pale brass-yellow, but on a fresh cleavage greyish-white. The mineral occurs with quartz and iron-pyrites on crevices in dacite; its locality is not stated (but is presumably Nagyag, Transylvania).

L. J. S.

**Apatite and Spodiosite.** FRANK K. CAMERON and W. J. McCaughey (*J. Physical Chem.*, 1911, 15, 463—470).—When tricalcium phosphate is dissolved in fused calcium chloride a granular, crystalline substance which has the formula  $\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCl}_2$  results. This is the chlorine analogue of spodiosite and is termed *chlorospodiosite*. It is also produced by dissolving natural chlorapatite in fused calcium chloride. When excess of dicalcium phosphate is dissolved in calcium chloride, the product is chlorapatite,  $\text{Ca}_3(\text{PO}_4)_2 \cdot \frac{1}{2}\text{CaCl}_2$ . Artificial fluorapatite mixed with fluorite is obtained by dissolving calcium fluoride in fused disodium phosphate.

The apatites, which are more soluble than the spodiosites, are formed on heating the latter to redness, hence spodiosites rarely occur in nature. Apatite, which is widely distributed in rocks and soils, has apparently been formed when the molten magma was strongly acidic, and was one of the first minerals to crystallise out. Apatite crystallises in hexagonal prisms, chlorapatite having bipyramidal ends and fluorapatite usually basal pinacoid ends. Artificial fluorapatite sometimes exhibits the peculiarity of re-entrant pyramidal ends or phantom crystals. Spodiosite is orthorhombic, chlorspodiosite being much less developed along the *c* axis than fluorspodiosite.

R. J. C.

**New Mineral [from Brazil].** J. M. DE PADUA E CASTRO (*Revista Chim.*, 1910, 6, 365—369).—This mineral, found in the State of Espírito Santo, Brazil, consisted for the larger part of material having D 4.511, and containing in addition to tantalic, niobic and titanic acids, and zirconia, about 30% of a metallic oxide (XO) of a yellow colour, which belonged to the group of the rare earths, but could not be identified with any of those known. Aluminium, glucinum, chromium, yttrium, cerium, lanthanum, didymium, and thorium were all excluded. The quantitative composition was found to be as follows:

Ta <sub>2</sub> O <sub>5</sub> , Nb <sub>2</sub> O <sub>5</sub> .	TiO <sub>2</sub> .	ZrO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	XO.	H <sub>2</sub> O.	Not estimated.*
89.5	20.0	1.0	3.0	50.0	3.2	3.3

\* Quartz, alumina, graphite, and silica soluble in alkali.

The mineral is not entirely uniform, but showed at certain points yellow particles of a schistose character consisting of quartz (90%), combined silicic acid (1.5%), ferric oxide (7%), and alumina (0.8%).

W. A. D.

**Composition of Potash Felspars.** PHILIPPE BARBIER (*Bull. Soc. franç. Min.*, 1911, 34, 117—123. Compare Abstr., 1908, ii, 704).—A reply to Vernadsky and Révoutsky (this vol., ii, 122).

L. J. S.

**Formation of Kaolinite in Some Coal-measure Shales of Northumberland.** R. COOKSEY BURTON (*Proc. Univ. Durham Phil. Soc.*, 1911, 4, 24—29).—Kaolinite occurs as white patches in clay-ironstone at Whitley Bay (anal. I); as a material replacing the calcite of fossil shells in shale at West Wylam Colliery; and on the surfaces of fissures in shale at the Duke Colliery, Ashington (anal. II). Under the microscope, it is seen to consist of silvery-white scales, only rarely with hexagonal outlines, which possess a perfect basal cleavage and give a biaxial interference-figure; sp. gr. 2.58. Anal. III, of the portion insoluble in hydrochloric acid of the clay-ironstone from Whitley Bay, shows an approximation to the analyses of the kaolinite. The material has evidently been formed by the action of carbon dioxide in solution, which has removed the ferrous carbonate

and more readily decomposed silicates, and caused the aluminium silicate to recrystallise:

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	H <sub>2</sub> O	Total
I. 40.91	41.53	—	trace	trace	trace	—	16.83	99.27
II. 46.82	39.44	—	—	—	—	—	13.93	100.12
III. 47.24	21.72	3.39	0.08	0.70	4.42	—	22.56*	100.11

\* Including organic matter.

L. J. S.

**Metamorphic Natrolite.** STANISLAUS J. THUGUTT (*Centr. Min.*, 1911, 405—411).—In weathered phonolite, occurring in contact with fresh basalt in a quarry between Sattelles and Schömitz, near Carlsbad, Bohemia, the minerals found in the cavities are, in the order of their formation, phillipsite, thomsonite, natrolite, and calcite. The natrolite forms radiating bunches of needles on a base of thomsonite. The needles exhibit a distorted development of their faces, and the oblique optical extinction of 5—6° indicates monoclinic symmetry. Analysis of the material gave the following results, which, after deducting lime, etc., as due to the presence of admixed thomsonite (12.15%), agree with the natrolite ratios: H<sub>2</sub>O: SiO<sub>2</sub>: Al<sub>2</sub>O<sub>3</sub>: Na<sub>2</sub>O = 2.18: 2.98: 1.00: 1.03:

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	K <sub>2</sub> O	Na <sub>2</sub> O	H <sub>2</sub> O	Total	Sp. gr.
45.83	27.32	1.68	0.04	15.17	10.72	100.76	2.24

The fact that the material is a mixture is also indicated by the microchemical colouring reactions with methylene-blue and with silver chromate. The natrolite when partly dehydrated by heating over a flame for a few seconds gives an intense blue with methylene-blue, or an orange-red colour with silver chromate (10% silver nitrate with 20% potassium chromate). If the heating is continued for seven seconds these colour reactions are not obtained. On the other hand, with the natrolite from Leitmeritz (*Abstr.*, 1909, ii, 1097) and some other localities the heating may be continued for a longer period of time, proving that the material is more stable. For the less stable form of natrolite from Schömitz, the name *epinatrolite* is suggested. This has also been detected in the phonolites of some other localities, and it is suggested that it owes its origin to the alteration of minerals of the sodalite group, whilst normal natrolite is a derivative of nephelite. In their morphological and optical characters, and in chemical composition, these two forms of natrolite exhibit no difference.

The suggestion of Brögger that natrolites with oblique optical extinction contain potash, does not apply in the material here analysed.

L. J. S.

**Optical Properties of Rose Beryl from Madagascar.** ALFRED LACROIX and ETIENNE RENGADE (*Bull. Soc. franç. Min.*, 1911, 84, 123—125).—The rose-coloured beryl, occurring in Madagascar as crystals of tabular habit, contains alkalis, more especially cesium, replacing the glucinum. Corresponding with the higher atomic weights of the replacing elements, there is an increase in the sp. gr.

and refractive indices of the beryl. New analyses are given of material from: (I) Vohidaby, and (II) Maharitra:

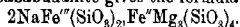
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	GIO.	FeO.	MnO.	CaO.	CaO.	Na <sub>2</sub> O.	Li <sub>2</sub> O.	Loss on ignition.	Total.
I. 62.70	30.30	1.04	trace	—	1.43	1.03	0.83	2.63	99.96		
II. 60.39	29.05	0.26	trace	0.34	4.56	0.24	2.00	2.23	99.07		

This material also gave the following results, which are compared with the results obtained by Duparc, Wunder, and Sabot (Abstr., 1910, ii, 312) and by Ford (Abstr., 1910, ii, 873) for rose beryl from Madagascar:

Locality.	Total alkalis.	Sp. gr.	$\alpha$ .	$\epsilon$ .	$\alpha-\epsilon$ .
Tsilaisina (Duparc) .....	0.92	2.716	1.5822	1.5760	0.0062
Vohidaby .....	3.29	2.75	1.5860	1.5795	0.0065
Madagascar (Ford) .....	4.98	2.79	1.59500	(1.58891)	(0.00609)
Maharitra .....	6.80	2.81	1.5996	1.5811	(0.0085)

L. J. S.

**A Variety of Riebeckite (Bababudanite) and Cummingtonite from Mysore.** WILLIAM FREDERICK SMEETH (*Records Mysore Geol. Dept.*, [1911], 9 [for 1907—8], 85—94).—The quartz-magnetite-schists of the Bababudan Hills in the Kadur district contain beds of cummingtonite, with, here and there, black radiating prismatic aggregates of a soda-amphibole closely allied to riebeckite, for which the name bababudanite is proposed. The quartz-magnetite-schists appear to have been derived from the decomposition of the amphiboles. Analysis I. of the bababudanite gives the formula



The mineral has a prismatic cleavage angle of  $56^\circ$ ; and it differs from riebeckite in having a slightly greater angle of extinction ( $\alpha : \epsilon = 7-9^\circ$ ), and in the character of the pleochroism ( $\alpha$  prussian-blue,  $\epsilon$  purple tending to violet,  $\epsilon$  yellow with tinge of green).

The cummingtonite is brown, due to ferruginous material along cracks, but when magnetite has been separated with a magnet and the material boiled with hydrochloric acid, it is perfectly colourless (anal. II.):

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO.	MnO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.	Sp. gr.
I. 54.43	2.10	15.79	5.02	0.08	1.04	12.11	0.32	6.34	0.40	98.31*	3.18	
II. 56.43	0.51	—	20.55	2.90	0.85	18.68	—	—	—	99.97	3.191	

\* Insol. in HF and H<sub>2</sub>SO<sub>4</sub>, 0.63; P<sub>2</sub>O<sub>5</sub>, trace; TiO<sub>2</sub>, nil.

L. J. S.

## Physiological Chemistry.

**The Causes of Absorption of Oxygen by the Lungs in Man.** C. GORDON DOUGLAS and JOHN S. HALDANE (*Proc. Roy. Soc.*, 1911, B, 84, 1—2).—During rest and under normal conditions, and



provided the blood is not more than about 25% saturated with carbon monoxide (experimentally added to the inspired air), the tensions of oxygen in the arterial blood and in the alveolar air are practically identical. Under such conditions, therefore, oxygen absorption occurs by diffusion alone. But when the percentage of oxygen in the inspired air is lowered sufficiently (or the saturation of the blood with carbon monoxide is increased sufficiently), the tension of oxygen in the arterial blood is much higher than in the alveolar air. During muscular work, especially when the air is poor in oxygen, the same effect is produced. Under these conditions, therefore, active secretion of oxygen inwards is taking place. In muscular work, it is considered that the pulmonary epithelium is stimulated to secrete oxygen inwards by the products of metabolism.

W. D. H.

**Influence of Inhalation of Oxygen on the Lactic Acid Produced during Hard Work.** ISRAEL FELDMAN and LEONARD E. HILL (*J. Physiol.*, 1911, 42, 439—443).—Inhalation of oxygen markedly lessens the excretion of lactic acid in the urine after hard work. The increased production of the acid which occurs when air is breathed is considered to be due to want of oxygen. The observations were made on man.

W. D. H.

**The Action of Intravenous Infusions of Saline Solutions on the Respiratory Exchanges.** FRITZ VERZAR (*Biochem. Zeitsch.*, 1911, 34, 41—51).—The method employed was the same as that used by Tangl. It was found that injection of even 0.75% sodium chloride caused an increase in the oxygen consumption when the kidneys were excluded from the circulation. This increase is less than the increase of carbon dioxide excretion; the injection of the saline solution causes, therefore, a diminution in the respiratory quotient. The experiments afford no explanation as to the mode of action of sodium chloride.

S. B. S.

**The Respiration of the Eggs of the Sea-urchin (*Strongylocentrotus lividus*) in Pure Sodium Chloride Solutions.** OTTO MEYERHOF (*Biochem. Zeitsch.*, 1911, 33, 291—302).—The amount of oxygen used up by the eggs was determined by Winkler's method. It was found that in sodium chloride solutions from somewhat less than two to more than four times as much oxygen was used up as in isotonic sea-water.

S. B. S.

**Action of Chloroform on Blood-Vessels.** J. ARGYLL CAMPBELL (*Proc. physiol. Soc.*, 1911, xxxiii—xxxiv; *J. Physiol.*, 42).—Schäfer and Scharlieb state that chloroform in oxygenated Ringer's fluid produces vaso-constriction, except in the kidney vessels. Embley and Martin, using the drug in oxygenated defibrinated blood, state that the main effect is vaso-dilatation. Both these results are confirmed. If the blood is not oxygenated, constriction occurs. Oxygenation makes no difference to the effect obtained when Ringer's fluid is employed.

W. D. H.

**Effect of Increased Temperature of the Carotid Blood.** V. H. K. MOORHOUSE (*Amer. J. Physiol.*, 1911, 23, 223—234).—Dogs were anaesthetised with urethane or morphine, and the carotid arteries enclosed in heaters through which a stream of hot water was kept flowing. The vertebral arteries were tied. The results of thus warming the brain are: (1) an increase in the heart's rate preceded by a primary decrease due to an increased vagus tone; (2) increase of blood in the periphery due to vaso-motor response, and (3) an increase in respiratory ventilation, which is usually due to an increased rate of breathing; but increase of depth may occur in respiration without increase, or even with decrease, in the rate. These differences are probably due to difference in activity of the sensory side of the respiratory mechanism.

W. D. H.

**The Influence of Intravenous Blood Transfusion on the Metabolism of Matter and Energy.** PAUL HÄRI (*Biochem. Zeitsch.*, 1911, 34, 111—146).—The effect of directly transfusing the blood from one dog into another was investigated, the respiratory exchanges, nitrogen and carbon output in the urine and faeces (the latter estimated by the Brunner-Messinger-Scholz dichromate method) being measured. Direct measurements of the heat developed by the animals were also made at the same time as that of the respiratory exchanges with the employment of a Rubner respiration calorimeter. The caloric values of the egesta were also measured in a Berthelot-Mahler calorimeter. It was found that the transfusion of blood into an animal caused an increased destruction of protein and apparently also a limitation of the fat consumption. In starving animals, when the amount of water ingested is the same before and after transfusion, there is a diminution of the water excreted after the transfusion; this is not the case with fed animals. There is a small increase in heat production after transfusion, due to the increased work of the heart.

S. B. S.

**Deamidation in the Blood of Normal Animals, and in Those Deprived of the Thyroid.** AN. K. MEDVEDEFF (*Zeitsch. physiol. Chem.*, 1911, 72, 410—448).—The course of the development and disappearance of ammonia in the blood in (1) normal animals; (2) animals in the state of inanition, and (3) after removal of the thyroid, is expressed by the equation  $dx/dt = (k_d - k_s)(a - x)$ , where  $k_d$  and  $k_s$  are the respective coefficients of velocity of the deamidation and synthetic processes. In the circulating blood of the animals of the first category,  $k_d = k_s$  and  $k_s = 0$ ; in those of the second category,  $k_d < k_s$  and  $k_s = 0$ ; in those of the third category,  $k_s = 0$  and  $k_d = 0$ . In the blood of animals of the first two categories, after bleeding, deamidase diffuses into the blood-plasma from the corpuscles; in those of the third category this does not occur, the amount of deamidase in it remaining constant.

W. D. H.

**Anti-coagulants on Frog's Blood.** HAROLD PRINGLE and JOHN TAIT (*Proc. physiol. Soc.*, 1911, xxxviii—xxxix; *J. Physiol.*, 42).—Most anti-coagulants of frog's blood (viperine venom, peptone,

novocaine, potassium oxalate and fluoride, neutral salts, and hirudin) preserve the shape of the spindle cells or thrombocytes, and prevent resetting of red-corpuscles around them. If calcium chloride is subsequently added, cytolysis of the thrombocytes and resetting of red-corpuscles begins in a few minutes. It is inferred that calcium is necessary for cytolysis of these cells.

W. D. H.

**The Scission of Esters in the Blood.** PETER RONA (*Biochem. Zeitsch.*, 1911, 33, 413—422).—The scission of tributyrin by blood was investigated by the method of surface-tension measurements already described by the author. The reaction was found to be unimolecular when carried out in a neutral solution (1 part mono-hydrogen and 7 parts dihydrogen sodium phosphate). The reaction rate was directly proportional to the quantity of ferment present. The optimum of the reaction was in the presence of the hydrogen ion concentration of the blood, and the rate diminished if this concentration be increased by using acetate mixtures, or mixtures containing larger quantities of the mono-hydrogen phosphate. Increase of alkalinity to a certain point also diminished the rate, but in this case accurate results were not obtainable, owing to the direct hydrolysing action of the hydroxyl ions.

S. B. S.

**The Blood of Ascidians. I. Vanadium Compound in the Blood-corpuscles.** MARTIN HENZE (*Zeitsch. physiol. Chem.*, 1911, 72, 494—501).—*Phallusia* was the principal ascidian worked with, but similar results were obtained with the blood of *Ascidia mentula*. The plasma contains only 0.2% of protein; it has  $\Delta - 2.12$ , whilst that of sea-water is 2.07. The blood-corpuscles are extremely acid to litmus; the acid being volatile with steam in part, and probably organic. On exposure to air the corpuscles turn yellowish-green to blue; the chromogen of the pigment is dissolved out of them by distilled water (it is also soluble in acetone), and in time turns brown. This is probably not due to oxidation; on incineration it yields about 15% of vanadic acid ( $V_2O_5$ ).

W. D. H.

**The Permeability of Blood-corpuscles in Physiological Conditions, Especially to Alkali and Alkali-earth Metals.** G. GRYNs (*Proc. K. Acad. Wetensch. Amsterdam*, 1911, 14, 122—123).—Polemical. A further discussion on Hamburger's results, especially on the way in which the calculations should be made.

W. D. H.

**Do the Individual Red-Blood Corpuscles of a Suspension of the Same Show Measurable Individual Differences?** LUDWIG DIENES (*Biochem. Zeitsch.*, 1911, 33, 268—274).—The method of investigation consisted in treating a suspension of the corpuscles with an amount of hypotonic salt solution insufficient to cause complete hæmolysis. The total solids and hæmoglobin content were estimated in the centrifuged residue, and the ratio of these two factors compared with the ratio in centrifuged untreated corpuscles. The two ratios were found to be the same, and the author gives the reasons for drawing the conclusion from these results that there are individual

differences in the blood-corpuscles, the chief reason being that it is unlikely that the hæmoglobin and other constituents are dissolved from the corpuscles in the same proportions.

S. B. S.

**The Proteins of Serum.** FERDINAND BREINL (*Arch. exp. Path. Pharm.*, 1911, 65, 309—314).—The relationships of the albumin and globulin of the blood-serum constitute a puzzling physiological problem. Cervello found that the administration of antipyrine increases the globulin and diminishes the albumin. This is confirmed. It is further shown that *in vitro* admixture of antipyrine with serum leads to the same result. The proteins were estimated by the "salting out" method. If the transformation is a real one, it is either assumed that it must be accompanied with a change of a part of the cystine of the albumin into glycine, since globulin contains glycine and albumin does not, and globulin contains less cystine than albumin.

W. D. H.

**The Chemical and Physical Changes in the Blood-Serum Taking Place During Starvation.** MICHAEL POLÁNYI (*Biochem. Zeitsch.*, 1911, 84, 192—204).—During starvation there is a diminution in the following factors: protein content, total solids, viscosity, and specific gravity. The surface tension increases. The content in ash increases during starvation, as does also the chlorine content measured directly, and indirectly by Wassmuth's calculations from the conductivity). The osmotic pressure also rises. The amount of it shows no regular variations. The concentration of the hydrogen ions increases.

S. B. S.

**Formation of Dental "Tartar" by Dissociation of the Carbo-phosphates of Saliva.** A. BARILLÉ (*J. Pharm. Chim.*, 1911, vii, 3, 582—585).—Nespoulous has recently extended the views expressed by the author (*Abstr.*, 1904, ii, 27; 1910, ii, 74, 523) as to the origin of bones and calculi by dissociation of carbo-phosphates, to explain the formation of dental tartar, and the present paper gives confirmatory experimental data. Saliva leaves 5 or 6 grams per litre of mineral matter, consisting of magnesium and calcium carbonates and phosphates, and gives a precipitate of these constituents when made alkaline or exposed to air, due to removal of carbon dioxide from dissolved carbo-phosphates in either case. Salivary calculi always contain calcium phosphate and carbonate. The mineral matter of dental tartar includes 70% of tricalcium phosphate and 8% of calcium carbonate, the presence of the former being due to the fact that decomposition of carbo-phosphates in the mouth usually occurs in presence of alkali.

T. A. H.

**Influence of Intake of Food on Gaseous Metabolism and Energy Production.** ALFRED GIGON (*Pflüger's Archiv*, 1911, 140, 39—592).—The organism carries on its fundamental metabolic processes independently of the moments when food is taken. The work of digestion has, however, a certain effect, and even in fasting the activity of digestive organs is a small factor. In ordinary

conditions of nutrition the taking of carbohydrate or protein produces intermediate effects. Sugar is in part changed into fat. Protein food also leads to the laying on of fat. Each constituent of the diet has a specific action both in the direction of energy production as well as in its metabolic effects. This specific action manifests itself whether the substances are given alone or mixed together.

W. D. H.

**The Action of Certain Sulphur Compounds on Metabolism and Excretion.** CHARLES O. JONES (*Bio.-Chem. J.*, 1911, 5 427—441).—In rabbits, sulphates in large amount lessen oxidative changes in the cells, by preventing exchange between them and the blood stream. As the sulphate is reduced this disappears, and a stage of stimulation accompanied by diuresis follows. There is a marked irritant action on the kidney cells. Purgation is not common. This sulphates which are quickly reduced in the body to sulphites act in the same way; so also do sulphites and sulphides if oxidising enzymes are abundant. If there is a deficiency of these enzymes, sulphites appear to unite with and neutralise the action of tissue enzymes; and sulphides appear to unite with some constituent of the cell itself, and to interfere with and ultimately stop all metabolic changes.

W. D. H.

**Fat Digestion.** STEFAN VON PESTHY (*Biochem. Zeitsch.*, 1911, 34, 147—169).—The hydrolysis of fats (emulsions of olive oil with gum arabic and water, and of egg-yolk with water) by means of the lipases of stomach (from dog and man) and pancreas was investigated by estimating, not only the fatty acids, but the glycerol formed in the process. The latter was determined by precipitation of the digestion mixture with phototungstic acid, removal of the excess of the latter by barium salt, removal of the excess of barium by carbon dioxide, and of the chlorine by silver hydroxide. In the filtrate from the various precipitates, the glycerol was estimated by the Zeisel-Fanto method. The same methods were employed for estimating the glycerol and fatty acids in the contents of the small intestine. It was found that the glycerol estimations yielded more trustworthy values than the fatty acids determinations, as the latter, for some unknown reason, showed irregularities in the case of egg-yolk. With pure fats, however, both factors gave fairly accurate numbers. The conclusion was drawn from the results obtained that the stomach contains a true lipase secreted from the mucous membrane, and that the scission of fat is not due to regurgitated enzymes from the intestine, as these lose their activity in the acid gastric contents; furthermore, in cases where regurgitation is known to take place, as in achylia gastrica and carcinoma, no scission of fat by the gastric contents was observed. In the intestine, both fat and glycerol were present, but not in the proportions corresponding with the chemical formula of fats.

S. B. S.

**The Influence of the Melting Point of Fats on their Rate of Disappearance from the Stomach.** FRANZ TANGELAND ALEXANDER ERDELYI (*Biochem. Zeitsch.*, 1911, 34, 94—110).—The fats, linseed oil

live oil, lard, and beef fat, were made into emulsions, in as nearly as possible the same way, by means of water and gum arabic, and introduced by a stomach-tube into the stomachs of dogs. In different animals, after various intervals, the content of the stomach in fat was estimated. This was done by administering to the animals at the desired intervals after ingestion of the fat, *apomorphine*, which causes the stomach contents to be vomited quantitatively. As the result of numerous experiments carried out in this manner, the conclusion was drawn that the rate of disappearance of emulsions of fats from the stomach is a function of their melting points and viscosities; the higher the melting point and the greater the viscosity, the more slowly they disappear from the stomach.

S. B. S.

**The Diastases.** IX. The Influence of Serum, Lymph, and the Expressed Juices of Organs on Diastatic Action. JULIUS VOHLGEMUTH (*Biochem. Zeitsch.*, 1911, 33, 303—314).—Serum accelerates the action of diastase to a much greater extent than can be accounted for by its content in sodium chloride. The accelerating action is not increased by allowing the serum to act on the diastase for a prolonged period, and it appears, therefore, that the diastase does not enter into combination with the accelerating substance, but that the latter forms a substrate for the action in the same way that sodium chloride does. The accelerating action can be detected when only very small quantities of serum are added, and serum obtained from all parts of the body of the same animal has an equal accelerating effect. Serum taken from an animal after a meal has a slightly greater effect than that taken from the animal before. The strongest activating effect is obtained by the sera from the dog, sheep, and rabbit; then follow the sera from man, rat, horse, ox, and goat. The diastase from all organs is activated by serum. The lymph and expressed juice from other organs also exert an accelerating effect. The accelerating substance is in all cases heat-stable and soluble in alcohol. The comparative accelerating effect of the expressed juices of several organs is investigated.

S. B. S.

**Carbohydrate Metabolism.** FELIX REACH (*Biochem. Zeitsch.*, 1911, 33, 436—448).—Raw meat increases the sugar output in a dog from which the greater part of the pancreas has been removed. This increase cannot be explained by assuming that with raw meat there is a greater utilisation of the food-stuff. The observation of Hédon was confirmed that phloridzin decreases the blood-sugar content in dogs with pancreatic diabetes. By this means the amount of blood-sugar can be reduced to the normal. It does not appear, therefore, that the diminution of the blood-sugar content in diabetes can be regarded as a favourable alteration in the metabolism disturbances. The influence of muscular work on the blood-sugar content was also investigated. There was found in nearly all cases an increase when the muscles passed from a condition of rest to one of activity, and in most cases a diminution when the muscles passed from a state of activity to one of rest.

S. B. S.

**The Metabolism of Starch when Introduced Parenterally.** FRITZ VERZÁR (*Biochem. Zeitsch.*, 1911, 34, 66—85).—If starch solutions be injected rapidly, starch will appear in the urine; the kidneys are therefore permeable to starch. With slow injections, on the other hand, no starch will appear in the urine. Both dogs and rabbits behave in this respect in a similar way. If the starch is injected slowly, it disappears rapidly from the blood. The intravenously injected starch is, in this case, entirely oxidised, a fact determined by the measurement of the respiratory exchanges. The same result was obtained whether the starch was injected into the jugular or portal vein. With dogs made diabetic with uranium nitrate, the injection of starch causes an increased output of sugar in the urine; this increase corresponds with the amount of starch injected. Starch appears, therefore, when injected, to be first hydrolysed to a sugar, which is then burnt. After partial extirpation of the pancreas, dogs will tolerate the injection of quantities of starch which are fatal to normal animals. This fact can be explained by the presence of larger quantities of diastase in the blood of those animals in which the pancreas has been partly removed.

S. B. S.

**The Resorption and Excretion of Starch Granules.** FRITZ VERZÁR (*Biochem. Zeitsch.*, 1911, 34, 86—93).—Experiments were carried out on human beings, dogs, rabbits, and rats. Starch granules, in the form of paste, were ingested. At intervals afterwards, the urine was collected, with stringent precautions to guard against any contamination, and centrifuged. The deposit was examined histologically, and found to contain starch granules, from which result the conclusion was drawn that the granules can pass from the intestine into the blood-stream, and then be excreted by the kidneys. These observations confirm those of Hirsch.

S. B. S.

**Creatine and Creatinine Metabolism in Dogs with Eck Fistula.** NELLIS B. FOSTER and HENRY L. FISHER (*J. Biol. Chem.*, 1911, 9, 359—362).—In dogs with Eck fistula, ingestion of creatinine was followed by a rise in creatinine excretion, and in one case by an increase of creatine excretion. This, however, was probably accidental. After ingestion of creatine, there is no rise in creatine output, and the rise in creatinine excretion was too small to be convincing.

W. D. H.

**Action of Gastro-Intestinal Juices on Nucleic Acids.** PAVEL A. LEVENE and FLORENTIN MEDIGRECEANU (*J. Biol. Chem.*, 1911, 9, 375—387).—The nucleic acids are mono- or poly-nucleotides, that is, compounds of phosphoric acid conjugated with a complex composed of carbohydrate and a base. During metabolism they undergo complete disintegration; how far this occurs in the process of digestion is uncertain, although London and Schittenhelm regard it as proved that in the intestine (but not in the stomach) decomposition occurs, which if complete, liberates purine bases, and if incomplete leads to the formation of nucleosides. In the present experiments the substances employed (given in order of increasing complexity) were inosin, cytidin, guanylic acid, pyrimidine nucleotides, yeast-nucleic acid, and thymus-

nucleic acid. The juices used were active, and were supplied by Pawloff. Inosin, guanosin, and cytidin were unchanged by gastric, pancreatic, and intestinal juices alone or in combination. Guanylic acid was changed by intestinal juice only, and the change was a detachment of the phosphoric acid from guanosine, the latter substance being precipitated in crystalline form. Pyrimidine-nucleotides underwent the same change under the influence of the same juice, but to a less degree. The nucleic acids from yeast and thymus were also attacked by intestinal juice only, and of the two that from yeast was most decomposed. It became soluble in glacial acetic acid; this is possibly due to cleavage into mono-nucleotides; phosphoric acid was also liberated.

W. D. H.

**Digestion and Absorption of Nucleic Acid in the Gastro-intestinal Canal.** II. E. S. LONDON, ALFRED SCHITTENHELM, and CARL WIENER (*Zeitsch. physiol. Chem.*, 1911, 72, 459—462).—The authors agree with Levene and Jacobs that the final splitting of nucleic acids occurs in the organs and tissues. If, however, guanylic acid is given to dogs, the chyme in the ileum contains guanosine; this was isolated and identified with certainty. It also was found after feeding on thymus-nucleic acid.

W. D. H.

**The Presence of Secretin During Fœtal Life.** HAROLD RINGE (*Proc. physiol. Soc.*, 1911, xl; *J. Physiol.*, 42).—Active secretin can be prepared from new-born kittens and some fetuses. The date of its appearance in fetal life is still undetermined.

W. D. H.

**Autolysis of the Brain.** FRIEDRICH SIMON (*Zeitsch. physiol. Chem.*, 1911, 72, 463—483).—Previous attempts to determine whether proteolytic, phosphatide-splitting or other enzymes are present in brain tissue have yielded uncertain and contradictory results. Calves' brain was employed in the present investigation, and chloroform used as an antiseptic; distinct evidence was found of the presence of autolytic enzymes; proteolytic products occur; the main question investigated, however, relates to phosphorised constituents; phosphorus is split off from organic union, and the amount of inorganic phosphates rises correspondingly; this is true for the brain constituents which are soluble as well as for those which are insoluble in alcohol and ether.

W. D. H.

**Carbohydrate Tolerance and the Posterior Lobe of the Hypophysis Cerebri.** EMIL GOERTSCH, HARVEY CUSHING, and CONRAD ACCOBSON (*Bull. Johns Hopkins Hospital*, 1911, 22, 165—190).—From experimental studies on animals, and clinical observations on man, the following conclusions are drawn. The secretion of the posterior lobe of the pituitary body is discharged into the third ventricle, and enters the blood-stream by way of the dural sinuses. The infundibulum and its stalk hold a reserve deposit of this secretion, and when this part is interfered with, a transient hyperæmia and glycosuria occurs; the fleeting glycosuria which often



accompanies fractures of the base of the skull is probably produced in this way. A short period follows in which the assimilation limit for ingested carbohydrates is lessened, and alimentary glycosuria is readily produced. This is succeeded by an enduring augmentation of tolerance for sugars, which is lowered by injection of posterior lobe extract. The sugar tolerance of normal animals is also lowered by such injections. The increased tolerance is accompanied by adiposity, and a subnormal temperature which indicates conversion of sugar into fat and a lessened power of oxidation. Injections of the posterior lobe extract conversely cause emaciation. Adiposity is not due therefore solely to deficiency in the secretion of the anterior lobe. W. D. H.

**The Chemistry of Hydrocephalic Liquid.** MICHAEL POLÁČEK (*Biochem. Zeitsch.*, 1911, 34, 205—210).—The following factors were determined from four cases of hydrocephalons: specific gravity, freezing point, electrolytic conductivity, hydrogen ion concentration, refractive index, viscosity, surface tension, total solids, protein, fat (by different methods), cholesterol, ash, water-soluble and water-insoluble constituents of ash, and sodium chloride. From the results, which are tabulated, the author draws the conclusion that the hydrocephalic liquid is probably lymph. S. B. S.

**Iodine in the Human Pituitary.** W. DENIS (*J. Biol. Chem.*, 1911, 9, 363—364).—Twenty-six human pituitaries were investigated, and in five of these cases iodide had been administered before death. In no case was even a trace of iodine obtainable. W. D. H.

**The Amino-acids in the Mature Human Placenta.** ARTHUR H. KOELKER and J. MORRIS SLEMONS (*J. Biol. Chem.*, 1911, 9, 471—489).—Approximately one-half of the fresh placenta is blood, the dried placental material is about 7% of the fresh weight. The hydrolytic products (amino-acids and ammonia, the results of estimation of which are given in detail) represent 31% of the organic matter. Placental tissue free from water and ash contains 14.9% of nitrogen. W. D. H.

**The Magnitude of the Work of the Liver.** FRITZ VERZÁR (*Biochem. Zeitsch.*, 1911, 34, 52—62).—Tangl's method was also employed in these experiments, in which the respiratory exchanges of curarised dogs before and after exclusion of the liver from the circulation, were measured. In this case it was not possible to exclude the liver entirely, Queirolo's operation being carried out, which consists in joining the vena cava with the portal vein. From the results, the conclusion is drawn that the liver utilises 12% of the total energy of the organism when muscular work is excluded by curare. There is also an increase in the respiratory quotient. S. B. S.

**Is the Activity of the Liver Indispensable for the Combustion of Sugar?** FRITZ VERZÁR (*Biochem. Zeitsch.*, 1911, 34, 63—65).—The respiratory exchanges were measured in curarised animals with the liver excluded from circulation by the metho

described in the previous paper, before and after injection of starch and dextrose solution. From the measurement of the increased oxygen consumption and carbon dioxide excretion, the conclusion was drawn that the injected substances were entirely oxidised, and that for the utilisation of carbohydrates it is not essential that they should be first converted into glycogen in the liver.

S. B. S.

**Influence and Rôle of Fatty Matters in the Catalytic Activity of Hepatic Extracts.** EUGÈNE CHOAY (*J. Pharm. Chim.*, 1911, [vii], 3, 525—534, 574—580).—Pigs' liver after extraction by chloroform is much more active, and after extraction by acetone slightly more active, than the crude liver towards hydrogen peroxide. The chloroform and acetone extracts are inactive. The increase of activity is not proportional to the quantity of inert matter removed, being greater for chloroform and less for acetone. It is suggested that chloroform removes the enveloping fats and lipoids from the ferments in the liver and thus renders the ferments more readily soluble, and that acetone removes only the more liquid fatty matters, leaving the solid ones surrounding the ferments, so that the latter pass less easily into solution in water.

In the second paper the effects of extraction by chloroform and light petroleum are compared. Extraction by chloroform again produced an increase in activity, whilst extraction with light petroleum caused a greater diminution in activity than extraction by acetone.

The activity of all these materials towards hydrogen peroxide varies with the acidity of the peroxide solution, and consequently the latter should be neutralised by barium hydroxide and a definite quantity of sulphuric acid then added.

T. A. H.

**The Independence of the Diastatic Action on the Lipoids.** EMIL STARKENSTEIN (*Biochem. Zeitsch.*, 1911, 33, 423—435).—No appreciable difference could be detected between the diastatic action of the liver when the material contained lipoids and when it had been extracted in a dried form by toluene, ether, or alcohol and toluene. The divergence of this result from that obtained by other authors may be perhaps due to the fact that the lipoids decolorise the iodine used in Wohlgemuth's method of estimation of the diastases. Egg-yolk extract and commercial lecithin, however, inhibit the diastatic action, and this result is probably due to the acid character of the preparations. The authors also quote experiments which negative Bang's conclusions as to the increase of diastatic action of the organs in puncture diabetes, and in other cases of experimental glycosuria. He draws the conclusion that diastatic action generally is independent of the presence of lipoids.

S. B. S.

**Uric Acid Metabolism in Rabbits.** H. ACKROYD (*Bio.-Chem. J.*, 1911, 5, 442—444).—The excised rabbit's liver perfused with Ringer's solution produces a small quantity of allantoin. Sodium urate added to the solution is converted quantitatively into allantoin. None of the allantoin so produced is further destroyed,

W. D. H.

**Pnein.** FR. BATTELLI and (Mlle.) LINA STANN (*Biochem. Zeitsch.*, 1911, 83, 315—339).—Pnein is a substance of unknown nature which accelerates the primary respiration processes of tissues, as this respiratory process weakens after the death of the animal. It can best be studied on the liver of the dog, the kidneys of ox, and the muscles of horse or ox, which on washing with water can be deprived of the pnein contained in them. It appears to be necessary for the primary respiration, as tissues freed from pnein by washing, lose the greatest part of the respiratory power. The primary respiration is due, therefore, to the concomitant action of pnein and a very labile substance. The greater the weakening of this process, the larger the quantity of pnein necessary to restore it. It appears to exist in all tissues, and is in especially large quantities in the muscles of ox and horse. Certain tissues contain *antipnein*, which can be separated from pnein by dialysis, or by precipitation of the nucleoproteins by acids. Milk, blood, bile, and urine do not contain pnein. It is not destroyed by the respiration of the tissues, and does not appear therefore to be an oxidisable substance. It is easily soluble in water, acids, and alkalis, is dialysable, and not destroyed on boiling. For its destruction, the liquid containing it must be heated at 200°. It is not altered by pepsin or trypsin, or by hydrogen peroxide or ferric chloride, although it is destroyed by the combined action of the last two substances. It is slightly soluble in alcohol, but insoluble in benzene and ether. It can be partly purified by repeated precipitation by alcohol. It has no influence on secondary respiratory processes, or on the oxidation of uric acid by alcohol, or succinic acid by animal tissues. By itself, it exerts no oxidative action, neither does it increase the oxidative capacity of hydrogen peroxide. S. B. S.

**Extractive Material of Ox Kidneys.** K. BEBESCHIN (*Zeitsch. physiol. Chem.*, 1911, 72, 380—386).—The following substances have been previously isolated from kidneys: purine bases, uric acid, carbamide, creatine, leucine, tyrosine, glycogen, and inositol. The author has succeeded in isolating betaine in the form of the compound,  $C_5H_{12}O_2NCl_6HgCl_3$ , m. p. 246—250°. The base was also identified by means of its chloride, aurichloride, and picrate, m. p. 183° (Tonani gives 180—181°).

The betaine was isolated from the fraction from which Gulewitsch and Krimberg obtained carnitine.

Carnosine, methylguanidine, and carnitine do not appear to be present in kidney extract. J. J. S.

**The Work of the Kidneys and the "Specific-dynamic action" of Food-Stuffs.** FRANZ TANOL (*Biochem. Zeitsch.*, 1911, 34, 1—40).—The method of investigation consisted in determining the respiratory exchange of dogs before and after the exclusion of the kidneys from the circulation, and from the differences of the carbon dioxide output and oxygen consumption when the kidneys are in action and when they are thrown out of action, calculating the work done by these organs. The respiratory exchanges were measured by a modification of the Zuns-Geppert method, and the animals were

curarised so as to exclude as much as possible muscular work. They were kept at constant temperature in specially devised thermostats, or when too large, on electrically heated tables. Artificial respiration was employed in all cases. It was found by this method that 8.7% of the oxygen utilisation and 5.1% of the carbon dioxide excretion were due to the kidneys, numbers which agree well with the determinations of Barcroft and Brodie. From these numbers it was calculated that 7.9% of the energy metabolism of the whole organism was due to the kidneys. It has been found by Zuntz that certain substances, such as urea, sodium chloride, and proteins, cause, after ingestion, an increase in the energy exchanges of the organisms. Experiments were performed to determine how far this "specific-dynamic" action is due to the kidneys. The energy exchanges of the animals after exclusion of the kidneys from the circulation were measured both before and after the administration of such substances. It was found that even after exclusion of the kidneys, the administration caused an increase of the respiratory exchanges, from which the conclusion was drawn that the "specific-dynamic" action of such substances was not due directly to their stimulating action on the kidneys.

S. B. S.

**Reflux from Intestine to Stomach.** E. PROVAN CATHCART (*J. Physiol.*, 1911, 42, 433—438).—That bile is frequently found in the stomach has been known since Beaumont's days; several recent workers have pointed out that the administration of fat provokes an increased reflux of the intestinal contents. In the present research regurgitation in dogs was produced by sodium oleate and hydrochloric acid (0.2—0.4%), which are both substances that lead to formation of secretin; water, dextrose, and urea (one experiment) produced no such effect; sodium carbonate, peptone, and Liebig's extract produced the effect in one experiment and not in the other. The stronger the acid used, the earlier does the reflux occur. The regurgitated fluid, as a rule, only enters the antrum pylori, owing to the activity of the prepyloric sphincter.

W. D. H.

**The Chemistry of the Contents of the Intestine.** RUDOLF BORHM (*Biochem. Zeitsch.*, 1911, 33, 474—479).—A part of the ileum with two blind ends, due to an operation for hernia fourteen years before the death of the patient, was removed in a *post-mortem* examination, and was found to be filled with solid contents which were not of faecal character. This contained in addition to nucleoprotein, a portion soluble in ether and light petroleum which was about 33% of the total solids, and was obtained in crystalline form. The melting point and polarisation indicated that this substance was dihydrocholesterol.

S. B. S.

**The Action of Sulphur on the Intestine.** THEODOR FRANKL (*Arch. exp. Path. Pharm.*, 1911, 65, 303—308).—The change of sulphur into hydrogen sulphide was not found to occur in the intestine; but it is partly oxidised into sulphurous acid, which stimulates the intestinal wall, and in some cases produces hyperæmia, the outcome being increase of peristalsis.

W. D. H.

**The Relation of Stimulation and Conduction in Irritable Tissues to Changes in the Permeability of the Limiting Membranes.** RALPH S. LILLIE (*Amer. J. Physiol.*, 1911, 28, 197—222).—A rapid increase in surface permeability is the critical change in stimulation. This implies that the stimulus (for instance, an electric current) alters permeability directly or indirectly. The stimulating current produces a depolarisation at the seat of stimulation, which at the break is at the cathode. This decrease of an already existing polarisation is probably the really critical change in stimulation, and the increase of permeability is secondary to it.

W. D. H.

**Estimation of the Indophenol Oxydase of Animal Tissues.** HORACE M. VERNON (*J. Physiol.*, 1911, 42, 402—427).—When the chopped tissues of rat and rabbit are mixed with  $\alpha$ -naphthol,  $p$ -phenylenediamine, and sodium carbonate, the velocity of indophenol formation is in direct linear proportion to the time, although this slows down after the first two hours. When the substrate contains  $M/100$ -naphthol and diamine, the amount of indophenol formed is proportional to the square of the quantity of enzyme; with  $M/150$ -substrate, it is proportional to the quantity of enzyme; and with  $M/400$ , to the square root of the quantity of enzyme. The tissues of the rat are richer in oxydase than those of the rabbit; heart muscle is richest of all, then follow tongue muscles and diaphragm, renal cortex, and cerebral grey matter. The oxydasic power of the tissues runs parallel with their degree of oxygen saturation.

W. D. H.

**Lactic Acid and Cardiac Muscle.** W. BURRIDGE (*Proc. physiol. Soc.*, 1911, xli; *J. Physiol.*, 42).—The diastolic stoppage of the frog's heart produced by lactic acid is considered to be due to a displacement of calcium and potassium salts. Such a heart recovers in Ringer's solution, or by suitable doses of potassium and calcium salts.

W. D. H.

**Nicotine and Curarised Muscles.** W. BURRIDGE (*Proc. physiol. Soc.*, 1911, xlii; *J. Physiol.*, 42).—Langley showed that nicotine produces a larger initial shortening in curarised than in non-curarised muscles. The tracings obtained by the author suggest that this is due to a fusion of two effects, a quick one followed by another of a variable rate of development.

W. D. H.

**The Significance of Imbibition Phenomena on the Onset and Passing Off of rigor mortis.** OTTO VON FÜRTH and EMIL LEXX (*Biochem. Zeitsch.*, 1911, 33, 341—380).—It has been shown that acids when not above certain concentrations greatly accelerate the imbibition capacity of gelatin and other proteins for water. The same is true for muscular and other tissue, and the first stage of the post-mortem changes of muscular tissue is therefore apparently an imbibition phenomenon. After a time, the muscular tissue, as the authors' experiments show, loses water, the maximum increase of weight taking place between twenty and thirty hours after death.

This loss is not due to the increase in acid, as this increase is shown not to exceed that amount of acid above which loss of water occurs instead of imbibition. These results were arrived at by the investigation of the imbibition phenomena both in lactic acid and phosphoric acid solutions. With the loss of water by the tissues, the *rigor mortis* passes off, and this change, as the experiments show, is not due to mere loss of water by unchanged tissues, as the increase of acidity is not sufficient for this explanation. The second stage is due rather to a gradual coagulation of the proteins, the coagulated proteins possessing, as the experiments show, a smaller imbibition capacity for water than do the natural proteins. There are therefore two distinct post-mortem changes, namely, the imbibition of water, due to setting free of lactic acid, which change is a reversible one, and later a coagulation, resulting in the formation of a protein with smaller imbibition capacity. The latter change is irreversible. By a study of the action of salts and other substances, two distinct actions could be discriminated, either the substances could act on the cells and accelerate lactic acid formation, and consequently the imbibition rigor, or they could coagulate the proteins and produce a coagulation rigor, corresponding with the second stage of normal post-mortem change.

S. B. S.

**Utilisation of Ammonium Acetate and Asparagin for Maintenance and for Production of Milk.** AUGUST MORGEN, CARL BEYER, and F. WESTHAUSER (*Landw. Versuchs-Stat.*, 1911, 75, 265—320. Compare Abstr., 1907, ii, 294).—The results of further experiments with sheep confirmed those previously obtained, indicating that with rations deficient in protein, but containing sufficient starch values, ammonium acetate and asparagine may be utilised, not only for maintenance, but for milk production.

When ammonium acetate or asparagine was given instead of protein, the yield of milk was reduced by about 20—25%, whilst with carbohydrate in the place of protein, the reduction in the yield was about 10—15% more.

As regards the effect of the different foods on the live weight, the weights increased on the whole throughout the whole experimental period.

The average proportion of the nitrogen in the forms of ammonium acetate and asparagine utilised for maintenance and milk production amounted to 32.2%.

The amounts of products of metabolism were normal with foods containing protein and with ammonium acetate and asparagine, whilst they were somewhat higher when carbohydrates were substituted for protein.

N. H. J. M.

**An Animal Alkaloid from Sterilised Milk kept under Specific Conditions.** N. D. MERKIEFF (*Zeitsch. physiol. Chem.*, 1911, 72, 347—362).—Milk sterilised at 102° has been subjected to the following different treatments: (1) Exposure to light and air, the mouth of the vessel being protected by a cotton-wool plug. (2) Exposed to air, but protected from light. (3) Exposed to light, but protected from air by sealing the neck of the vessel. (4) Protected from both light and air.

The following determinations were made of the original sterilised milk and of a specimen kept for three years under the first three sets of conditions: reaction, sp. gr., fat, casein, albumin, lactose, ash, dry residue. After exposure to the conditions 1, 2, and 3, the milk had a sharp, unpleasant smell, the fat had diminished some 85% and a solid layer had formed on the surface. From each of the three samples an alkaloid,  $C_{38}H_{60}O_6N$ , was isolated. From 2 litres of milk under conditions 1, 0.562 gram; under conditions 2, 0.280 gram; and under conditions 3, 0.173 gram were isolated. The alkaloid was not formed under conditions 4. The alkaloid forms an amorphous powder, m. p.  $38^\circ$ , and begins to volatilise at  $52^\circ$ . It dissolves in most organic solvents with the exception of benzene, is charred by concentrated sulphuric acid, and gives an intense red coloration with hydrochloric acid. It yields precipitates with solutions of mercuric iodide, potassium iodide and iodine, mercuric chloride, potassium cadmium iodide; oxalic acid or picric acid in ether; tannic acid and platonic chloride. When injected in the form of an emulsion into guinea-pigs, it acts as a strong poison. Specimens of sterilised milk kept for four years and eleven months protected from air and light (conditions 4) contained no alkaloid, and had no poisonous properties. J. J. S.

**Sex and Metabolism.** R. A. KRAUSE and WILHELM CRAMER (*Proc. physiol. Soc.*, 1911, xxxiv—xxxv; *J. Physiol.*, 42).—The urine of women differs qualitatively and quantitatively from that of men; details will be published later. The point here emphasised is a tendency to creatinuria and a high ammonia excretion. Creatine occurs in the urine of normal women (on a creatine and creatinine-free diet) during and for some months after pregnancy, and also in the menstrual period. W. D. H.

**Process of Acid Excretion.** LAWRENCE J. HENDERSON (*J. Biol. Chem.*, 1911, 9, 403—424).—Like temperature and osmotic pressure, the normal neutrality or alkalinity [ $(OH^-)_{38} = 7 \times 10^{-7}N$ ] is adjusted and kept constant by a mechanism within the body. The acid end-products of metabolism take up alkali from blood and protoplasm; this tends to disturb the normal protective equilibrium between bases and acids, but is held in check by the kidney, which in urine formation acts in the reverse way and restores the alkali to the blood which had served as a carrier of acid. The quantity of acid excreted is measured by the amount of alkali which must be added to the urine in order to obtain the reaction of blood plus the urinary ammonia, and the method used for this purpose is described in full. The elaboration of ammonia and the presence of phosphoric acid as an end-product of metabolism make possible the excretion of acid; regulation of ammonia production and of the ratio of the acid to the alkaline phosphates of the urine are the means of regulating the acid excretion. W. D. H.

**Glycosuria and Sucroseria in a Healthy Man, following the Ingestion of 100 Grams of Sucrose.** J. L. E. GOFF (*Compt. rend.*, 1911, 152, 1785—1787).—The author holds the view that diabetes is increasing in France, and that this is due to an increase

in the consumption of sucrose. This opinion is supposed to receive support from experiments carried out on twenty-two subjects in whom there was no previous history of glycosuria. Each was given 100 grams of sucrose in the morning, and the urine examined after four hours. Dextrose was present in twenty instances (0.4—5.27 grams per litre), and sucrose was detected in every case (0.09—7.9 grams per litre).

W. O. W.

**The Influence of Phenylcinchoninic Acid (Atophan) on Purine Metabolism.** EMIL STARKENSTEIN (*Arch. exp. Path. Pharm.*, 1911, 65, 177—196).—This drug has been recommended for use in the uric acid diathesis. It increases the amount of uric acid excreted. In animals this is accompanied by a corresponding fall in the excretion of allantoin, and it probably acts by lessening oxidative processes that lead to allantoin formation. In man, however, this explanation does not hold; it is the endogenous uric acid which is increased, and the drug probably exerts an influence on the catabolism of nucleo-protein.

W. D. H.

**The Effects of Potassium Salts on the Circulation and on Plain Muscle.** G. C. MATHISON (*J. Physiol.*, 1911, 42, 471—494).—Intravenous injection of potassium salts causes a fall of arterial pressure, followed if the dose is not too large by a rise. The fall is due to action on the heart, and recovery is facilitated by washing it out with normal saline solution. Intra-arterial injection of potassium chloride causes in decerebrate and spinal animals, and in animals with the spinal cord destroyed, an immediate rise of pressure, which is due in part to excitation of vaso-motor centres, and in part to a direct effect on the muscular coat of the arteries, since it occurs when the nerve-endings are paralysed with ergotoxine. Skeletal muscle centres in the spinal cord are first excited, then depressed, and plain muscle in uterus and oesophagus is markedly contracted.

W. D. H.

**Chloroform and Reversal of Reflex Effects.** CHARLES S. SHERRINGTON and (Miss) S. C. M. SOWTON (*J. Physiol.*, 1911, 42, 383—388).—Reversal of reflexes under chloroform has been hitherto mainly studied in reference to blood-pressure effects. It is now shown that the same thing may occur in reflexes carried out by skeletal muscles.

W. D. H.

**Action of Methyl Alcohol in the Organism.** ADOLF FORSTER (*Bied. Zentr.*, 1911, 40, 431; from *Zeitsch. Spiritusind.*, 1910, 33, 2).—The stronger physiological action of methyl alcohol as compared with ethyl alcohol is perhaps due to impurities hitherto not detected.

N. H. J. M.

**The Toxic Action of Methyl Alcohol.** LOUIS LEWIN (*Chem. Zentr.*, 1911, i, 672; from *Apoth. Zeit.*, 1911, 28, 54—55).—The author gives many instances of the extraordinary toxicity of methyl alcohol which follows both inhalation and ingestion through the stomach. Of sixty-three hens' eggs, after injection of ethyl alcohol, 11.1% did not develop at all, 34.93% developed monstrosities; after



injection of methyl alcohol, 11.11% did not develop, whereas 65.49% gave rise to monstrosities.

S. B. S.

[Physiological] Action of Tetramethylammonium Chloride. CHARLES R. MARSHALL (*Proc. physiol. Soc.*, 1911, xxxvii—xxxviii; *J. Physiol.*, 42).—This substance temporarily inhibits respiration, mainly owing to its paralysing action on the nerve-endings in the respiratory muscles.

W. D. H.

Inactivation of Adrenaline *in vitro* and *in vivo*. WILHELM CRAMER (*Proc. physiol. Soc.*, 1911, xxxvi; *J. Physiol.*, 42).—Adrenaline is completely inactivated by a few minutes' contact with dilute formaldehyde, and this is probably due to an amino-group in the adrenaline molecule. Epinine (3:4-dihydroxyphenylethylmethylamine) is similarly affected. Pituitrine is not, and is therefore not a primary or secondary amine. Tissue extracts which lower blood-pressure are also unaffected by formaldehyde. It is suggested that the disappearance of adrenaline *in vivo* is due to a similar reaction with metabolic products.

W. D. H.

The Mechanism of the Action of Adrenaline. L. LICHTWITZ (*Arch. exp. Path. Pharm.*, 1911, 65, 214—224).—Adrenaline is known to act as a stimulus of the sympathetic system. Reasons are advanced for believing that the secretion of the suprarenal is not distributed by the blood, but by the nerves themselves, the secretion being poured into the sympathetic portion of the suprarenal bodies. Among the experiments adduced in favour of this view, the following may be mentioned. If the drug is injected into a frog's leg which is in connexion with the rest of the body by the sciatic nerve only, general effects on the rest of the body (the pupil, for instance) are observable.

W. D. H.

The Pharmacological Action of Some Halogen Substitution Products of Iminazoles [Glyoxalines]. KARL GUNDERMANN (*Arch. exp. Path. Pharm.*, 1911, 65, 259—283).—The great physiological importance of the halogens really dates from the discovery that iodine may be an integral part of organic compounds in the organism (as in thyreo-globulin), and from what has been found later, namely, that in iodised proteins the iodine is found united in certain of the merged cleavage products, such as tyrosine and tryptophan. It is now shown by experiments on bacteria, moulds, and animals that bromine-substitution products of glyoxaline (iminazole) are more toxic than the corresponding iodine compounds; 0.2 gram of 2:4:5-tribromoglyoxaline given by the mouth killed a dog weighing 6.5 kilos. in two hours. The most poisonous of the numerous iodine products examined is 4-iodo-5-methylglyoxaline; then follows 4:5-diiodo-2-methylglyoxaline, whilst 2:4:5-tri-iodoglyoxaline is relatively non-toxic. 1:2:4:5-Tetraiodoglyoxaline and tetraiodohistidin anhydride have little or no action, but it is difficult to ascertain how much of these are absorbed in the intestine. It is hoped that continuation of this work may throw light on the way iodine combined in the thyroid.

W. D. H.

**The Action of Morphine on the Heart.** A. A. J. VAN EGMOND (*Arch. exp. Path. Pharm.*, 1911, 65, 197—213).—Text-book statements as to the effect of morphine on the heart are brief and contradictory. In dogs, 0.04 mg. per kilo. of body-weight slows the heart, and this effect is more marked with larger doses. If, as sometimes occurs, this is preceded by quickening of the pulse, this is due to nausea, not to the drug. The slowing of the pulse is accompanied by fall of blood-pressure. The effect is excited on the vagus centre, and can be counteracted by division of the vagi, or by atropine. In cats, sometimes the heart is quickened, sometimes slowed; this is attributed to action on the vagus centre. In rabbits there is no certain effect on the heart at all. On the isolated cat's heart the contractions are strengthened by morphine. W. D. H.

**The Pharmacology of Certain Organic Mercury Compounds. The Action of Metallic Poisons.** FRANZ MÜLLER, WALTER SCHOELLER, and WALTHER SCHRAUTH (*Biochem. Zeitsch.*, 1911, 33, 381—412).—As the result of the investigation of the action of a large number of mercury compounds on cats and dogs, including several in which the mercury is directly combined with the carbon atom, the authors draw the conclusion that intoxication is not due directly to the mercury ion itself, as such an ion is not capable of existence in a medium containing protein. Of the metallic organic compounds, the sodium salts of the mercury dicarboxylic acids (with the metal directly combined with carbon) exert no toxic action when intravenously injected. The corresponding mercury hydroxyl compounds, on the other hand, exert a distinct toxic action, which is to be regarded as the action of the whole molecule and not of the ion alone. Death follows in these cases, as in all other cases of poisoning by mercury compounds after a typical paralysis of the vessels, or heart, or both. If, however, sub-toxic doses be given intravenously, the molecular action of the compound is first exerted, causing distinct symptoms of central origin; these rapidly disappear, and are followed by a third stage with the ordinary phenomena of chronic mercury poisoning (nephritis, enteritis, etc.). The chronic poisoning is a resultant of the rate of elimination and the rate of destruction of the compounds in the body (that is, the rate at which the mercury is set free from combination with the carbon in the compound). The latter factor runs parallel with the rate of formation of mercuric sulphide by ammonium sulphide. In the decomposition of these mercury carbon compounds an organic chloromercury compound is formed as an intermediate product. S. B. S.

**The Antagonism of Acids by Salts.** JACQUES LOEB and HARDOLPH WASTENEYS (*Biochem. Zeitsch.*, 1911, 33, 489—502).—The toxic action of acids on *Pundulus* can be antagonised by neutral salts. The coefficient of antagonism NaCl/acids is the same for hydrochloric and nitric acids, namely, 1/166; for butyric acid it is 1/100, and for acetic acid 1/33. For different concentrations of butyric acid the coefficient salt/acid is nearly constant. For different concentrations

of nitric acid there are larger variations, due possibly to the fact that the concentration intervals of the salt were not sufficiently small. The antagonistic action of calcium chloride is eight to eleven times as large as that of sodium chloride.

S. B. S.

**The Antagonistic Action of Sodium to Potassium Chloride.** JACQUES LOEB and HARDOLPH WASTENEYS (*Biochem. Zeitsch.*, 1911, 33, 480—488).—Whereas, in the case of *Fundulus*, it is possible fully to antagonise potassium chloride in the concentration in which it occurs in sea-water by sodium chloride, it is not possible completely to antagonise the sodium salt in the concentration in which it occurs in sea-water by the potassium salt; this can only be completely accomplished by calcium chloride. Sodium chloride solutions of greater concentration than 5/8 *m* cannot be antagonised by potassium chloride, and when the concentration is greater than 7/8 *m*, complete antagonism cannot be brought about by calcium chloride. The coefficient of antagonism NaCl/KCl is about 125 to 250, whereas the coefficient of antagonism KCl/NaCl is 1/15 to 1/17. If the concentration of sodium salt exceeds the latter limits the fish will die from sodium poisoning; if the concentration of the potassium salt exceeds the former limits, it will die from potassium poisoning. S. B. S.

**The Toxicity of the Fatty Acids and other Decomposition Products of the Fats.** THOMAS BOKORNY (*Chem. Zeit.*, 1911, 35, 630—632).—The toxic action of decomposed fats can be ascribed to the formation of the free fatty acids and other products of decomposition, glycerol, of course, forming an exception. From butyric acid upwards all the fatty acids are poisonous, in so far as they are soluble in water. The aldehydes are also poisonous, in some cases very markedly so, whereas the ketones are not so poisonous.

The poisonous action of a fat may not always be ascribed to the presence of decomposition products, since it is possible that it may be mixed with a poisonous substance which belongs neither to the fatty acids nor to the aldehydes.

T. S. P.

**Toxicity of Two New Nitriles and the Antitoxic Action of Sodium Thiosulphate towards One of Them.** ALEXANDRE DESGREZ (*Compt. rend.*, 1911, 152, 1707—1709).—From experiments on rabbits the toxic doses of Moreu and Bongrand's cyanoacetylene (this vol., i, 22) and dicyanoacetylene (Abstr., 1910, i, 159) are found to be 180 and 37 times as great as that of acetonitrile. It requires 2.65 grams of acetonitrile per kilogram of body-weight to produce death in ten minutes. Sodium thiosulphate in doses of 2 grams per kilogram has a protective influence in the case of dicyanoacetylene, but not in that of cyanoacetylene. W. O. W.

**The Influence of Poisons on the Catalase and the So-called  $\psi$ -Peroxidase Content of the Blood.** F. DUNCKER and ALX. JODLBAUER (*Biochem. Zeitsch.*, 1911, 33, 253—267).—The catalase was estimated by determining the amount of hydrogen peroxide decomposed by a given quantity of blood in a given time. The

$\psi$ -peroxydase content was determined by estimating the amount of carbon dioxide evolved when a given solution of pyrogallol was treated with a given amount of blood in a current of oxygen. The hæmoglobin content was also estimated. To rabbits were administered various poisons, and the examinations of the blood were made before, and at stated times after, the administration of the poison. Hydrocyanic acid caused a small diminution of the catalase content. Arsenic in non-toxic doses in ill-nourished animals can cause an increased catalase content of 22%. In well-nourished animals no change was observed. Arsenic in toxic doses had hardly any effect on the catalase content, although it caused a diminution of the hæmoglobin and  $\psi$ -peroxydase. Hydrogen arsenide caused a large diminution of catalase, hæmoglobin, and  $\psi$ -peroxydase. Phosphorus and chloral hydrate both cause a diminution of the catalase content; the other two factors are not appreciably altered. The alterations of the catalase content are independent of the alterations in the hæmoglobin; the alterations in the amounts of  $\psi$ -peroxydase run parallel with the changes in the hæmoglobin content.

S. B. S.

Experiments Serving to Explain the Parallelism between the Glycogenic Function and the Antitoxic Function of the Liver. ENRIQUE IGLESIAS (*Anal. Fis. Quim.*, 1910, 8, 421—426).—The experiments were made by injecting into the peripheral vein of a rabbit known weights of different poisons mixed with glycogen; the weights of the poison taken had been found to prove fatal in rabbits of the same body-weight when injected in the absence of glycogen. The substances experimented with were ammonium chloride, ammonium carbonate, morphine hydrochloride, cocaine citrate, and antipyrine, in solutions varying from 1% to 10% concentration. In nearly all cases, the rabbits showed marked symptoms of poisoning, but in most cases recovered. It is suggested that the glycogen acts as an antitoxin by combining with the poison in the blood, thus rendering it less diffusible and preventing it from permeating the walls of the cells so rapidly as to disturb the existing equilibrium therein. Glycogen may also act as a source of energy which enables endothermic degradation changes to occur within the cell more rapidly than usual, so that the partly killed cell receives help in eliminating the poison.

W. A. D.

### Chemistry of Vegetable Physiology and Agriculture.

$\beta$ -Alanine as a Bacterial Aporrhagma. D. ACKERMANN (*Zeitsch. Biol.*, 1911, 56, 87—90).—So far the only known aporrhagma (that is, a substance split off by biological action) of aspartic acid is succinic acid. This originates from aspartic acid by the action of putrefactive bacteria. It is probable that malic acid is split off from aspartic acid in plant life, but this is at present only a hypothesis. The experiments

now recorded show that, accompanying the succinic acid in putrefying aspartic acid,  $\beta$ -alanine is also present.

W. D. H.

**Rôle of Mineral Substances in the Formation of the Anthrax Protease.** JEAN BIELICKI (*Compt. rend.*, 1911, ii, 152, 1875—1877).—The proteolytic activity of anthrax bacteria depends to a considerable extent on the mineral constituents of the medium in which the organism has been cultivated. A culture taken from an asparagine solution containing calcium salts liquefies gelatin more rapidly than one from which these are absent, whilst salts of potassium, sodium, ammonium, and magnesium have an inhibitory effect on the subsequent activity. In experiments on the liquefaction of coagulated egg-albumin, the salts showed precisely the contrary effect, those of the alkalis favouring proteolysis, those of calcium hindering it. The salts are not effective in either case if they have been added to the culture already well developed in a pure medium.

W. O. W.

**The Biological Stimulative Action of Natural Humus.** THEODOR REMY and GEORG RÖSING (*Centr. Bakt. Par.*, 1911, ii, 30, 349—384).—Earlier results obtained by Krzemieniewski (*Abstr.*, 1909, ii, 335) were confirmed, and the relation between soil or soil humus and the power of nitrogen fixation by *Azotobacter chroococcum* was investigated. The stimulative action possessed by these substances was shown to be due, not to the humus itself, but to the small amounts of iron and silicates contained therein. The value of the iron depends largely on the form in which it is supplied. Ferric hydroxide held in solution by sucrose is very effective, whilst ferric silicate is also good. This accounts satisfactorily for the favourable action of basic slag on the nitrogen-fixing power of *Azotobacter*.

The optimum amount of iron was found to be 15 mg.  $\text{Fe}_2\text{O}_3$  for each gram of mannitol supplied; of this, only about 1 mg. is actually assimilated by the organism.

This distinct difference between optimum requirements and assimilated iron suggests a possible action of iron compounds in increasing the amount of oxygen in the cultures, and thus leading to increased assimilation of nitrogen.

H. B. H.

**Biochemical Study of *Proteus vulgaris*, Hauser.** CHRISTIAN A. HEETER and CARL TEN BROECK (*J. Biol. Chem.*, 1911, 9, 491—511).—In cultures, *Proteus vulgaris* ferments dextrose and sucrose, but not lactose; it destroys some native proteins, producing ammonia, primary amines, hydrogen sulphide, fatty acids of high molecular weight, aromatic hydroxy-acids, indole, and indoleacetic acid; it does not produce phenol, scatole, mercaptan, alcohols, aldehydes or ketones. If given to animals, the effects vary greatly, depending on the virulence of the organisms and the nature of the diet. The bodies of the organisms precipitated by alcohol contain a toxic material which is thermostable.

W. D. H.

**Assimilability of Different Carbohydrates by Different Yeasts.** P. LINDNER and K. SAITO (*Bied. Zentr.*, 1911, 40, 418—420; from *Woch. Brauerei*, 1910, 27, 509; *Zeitsch. ges. Brauw.*, 1910, 33, 626).—Maltose is the most readily assimilated sugar, and

very rarely fails to be utilised. Lactose, on the other hand, is only assimilated in isolated cases. Dextrin is frequently assimilated, but only to a small extent. Sucrose is of less importance in assimilation than glucose and levulose. Raffinose and arabinose occasionally give moderate growth. Dextrose and levulose are usually only moderately assimilated, if at all; in some cases when dextrose is assimilated, levulose is not, and vice versa.

*Schizosaccharomyces octosporus* was the only yeast which failed to assimilate any of the sugars employed, in presence of asparagine. *Saccharomyces Ludwigii* ferments dextrose, levulose, and sucrose vigorously, but does not assimilate them. N. H. J. M.

Influence of Humates on Micro-organisms. E. KAYSER (*Compt. rend.*, 1911, 152, 1871—1873. Compare this vol., ii, 648).—It is possible that the disease affecting ciders known as greasiness is due to insufficient washing of the apples from earthy material. It has been found that soluble humates from soil favour the development of the ferment to which the disease is due, probably by acting as an aliment for the organism, and not merely as a stimulant to its activity. W. O. W.

Utilisation of Aucubin by *Aspergillus niger*. HENRI HERISSEY and C. LEBAS (*J. Pharm. Chim.*, 1911, [vii], 3, 521—525. Compare Abstr., 1894, ii, 109; 1896, ii, 321; 1902, i, 634, and Pariewitsch, Abstr., 1899, ii, 683).—It is shown that the glucoside aucubin may be utilised by a mould, such as *Aspergillus niger*, but only when hydrolysis of the glucoside is effected by acids simultaneously present, or when there is enough mould tissue present to secrete hydrolytic enzymes in some quantity. Thus *Aspergillus niger* continues to grow in aqueous solutions of aucubin, and conidia of the mould develop and grow in acid nutrient media containing aucubin as the source of carbohydrate, but in neutral nutrient media containing aucubin, development of the conidia takes place very slowly. The dextrose produced from the glucoside is used by the mould, but it is doubtful whether the aucubigenin is so used. T. A. H.

Assimilation of Atmospheric Nitrogen by Higher Plants. EVA MAMELI and GINO POLLACCI (*Atti R. Accad. Lincei*, 1911, [v], 20, 680—687. Compare Abstr., 1910, ii, 645).—The authors have grown sterilised seeds of *Acer negundo*, *Solanum nigrum*, *Cucurbita pepo*, *Raphanus sativus*, and *Polygonum fagopyrum* in sterile nutrient media either free from nitrogen or containing a known amount of this element, and covered with bell-jars containing sterilised air exempt from ammoniacal, nitrous, nitric, and organic nitrogen. Determination of the weights of the plants obtained and estimation of the amounts of nitrogen in them and in the media employed show that, in all cases, atmospheric nitrogen is assimilated by these plants. In those experiments where large amounts of nitrogen were supplied in the media, little free nitrogen was taken up from the air; whilst, where the media contained but little nitrogen, which was all, or nearly all, utilised by the plants, larger amounts of atmospheric nitrogen

were assimilated. The results indicate that all plants, from the algae to the phanerogams, are able to assimilate atmospheric nitrogen.

T. H. P.

[Assimilation of Carbon by Plants.] LÉON MAQUENNE (*Compt. rend.*, 1911, 152, 1818—1819).—*Aspidistra*, which, according to Cailletet (this vol., ii, 642), are plants deriving most of their carbon from organic substances in the soil, are found to decompose regularly 0.03 c.c. of atmospheric carbon dioxide per hour per sq. cm. of surface during cloudy weather. This is slightly above the normal amount for herbaceous plants under like conditions. It follows that plants, such as ferns, which flourish in subdued light do not differ essentially from those which require sunlight for the satisfactory assimilation of carbon.

W. O. W.

The Fermentative Oxidation of Oxalic Acid. W. ZALESKI and A. REINHARD (*Biochem. Zeitsch.*, 1911, 33, 449—455).—Wheat seeds contain a ferment or catalyst, in the presence of which oxalic acid is oxidised to carbon dioxide. The reaction proceeds best with 1% solutions; in 3% solutions of the acid, the action ceases. Seeds previously heated or treated with methyl alcohol lose the oxidative action. The process does not, however, depend on the living condition of the seeds, as those treated with ether are also active. Finely powdered pea seeds and wheat embryos do not exert the same action, and the authors call attention to the differences in the respiratory processes between these and the wheat seeds.

S. B. S.

The Law of the Minimum and the Conclusions to be Drawn from It. EILHARD A. MITSCHERLICH (*Landw. Versuchs.-Stat.*, 1911, 75, 231—263).—The law of minimum (*Landw. Jahrb.*, 1909, 38, 557) is a logarithmic function. It requires new, exact vegetation experiments similar to Hellriegel's sand cultures.

N. H. J. M.

Chemical Differentiation of Species. MURIEL WHELDAL (*Bio.-Chem. J.*, 1911, 5, 445—456).—This is a preliminary attempt to co-ordinate the organic compounds occurring in plants with a view to the chemical differentiation of species. Many chemical compounds, for instance, certain alkaloids, are peculiar to certain species of plants. Lists are given of the principal groups of chemical compounds and of the plants in which they occur.

W. D. II.

Diffusion of Saline Substances through Certain Vegetable Organs. GUSTAVE ANDRÉ (*Compt. rend.*, 1911, 152, 1857—1860).—Potatoes immersed in sodium chloride containing formaldehyde as a preservative take up the salt in considerable amount, but this is slowly eliminated by exosmosis when the tubers are placed in distilled water. Untreated potatoes similarly lose about 40% of their naturally-occurring sodium chloride under the same conditions. All the chloride would probably be lost after a sufficiently long immersion in water.

W. O. W.

**Genesis of the Alkaloids in Plants.** GIACOMO L. CIAMICIAN and CIRO RAVENNA (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 614—624. Compare Abstr., 1908, ii, 773; 1909, ii, 604; 1910, ii, 234).—The authors have investigated the effect on the formation of alkaloids in *Datura* and the tobacco plant of inoculation, by the method previously described, with pyridine, piperidine, and pyrrolecarboxylic acid, and, in the case of tobacco, also with asparagine, ammonia, and certain non-nitrogenous compounds, such as dextrose and phthalic acid.

Pyridine has no specific influence in increasing the amount of alkaloid formed; in the tobacco plant, ammonia produces the same effect as pyridine. When asparagine is employed, the greatest yield of alkaloid is obtained. The amount of nicotine in the tobacco plant is also increased by making an aperture in the outer skin similar to that by means of which inoculation is effected and then closing it with paraffin wax. Dextrose also determines a considerable increase in the formation of nicotine. With phthalic acid, the increase is so small that, allowing for the effect of merely making an aperture, this compound actually seems to diminish the quantity of nicotine produced.

The results support the view that the vegetable alkaloids have their origin in amino-acids, and also Winterstein and Trier's supposition (*Die Alkaloide*, Berlin, 1910), that the bases, such as lysine and ornithine, formed from amino-acids are utilised by plants for the synthesis of alkaloids.

T. H. P.

**The Chemical Composition of the Root of *Asclepias vincetoxicum*.** GEORGES MASSON (*Chem. Zentr.*, 1911, i, 1065; from *Bull. Sci. Pharm.*, 1911, 18, 85—89).—After extracting the fat and a resin with light petroleum, a saponoid together with sugar can be obtained from the dried root by extraction with 60% alcohol. This is an acid which is insoluble in water, and can be obtained from its sodium salt by dialysing against acidified water. The free *asclepiac acid* is an optically inactive, amorphous, yellow powder, m. p. 90—91°, which on hydrolysis with 0.5% alcoholic sulphuric acid undergoes scission into reducing sugar, or a bright red, amorphous powder, insoluble in water.

S. B. S.

**Action of Cold, of Chloroform and Ether on Eupatorium ripulinerve.** EDOUARD HECKEL (*Compt. rend.*, 1911, 152, 1825—1827. Compare Pougnet, Abstr., 1910, ii, 993; this vol., ii, 528).—This plant does not contain a preformed odorous substance, but the odour becomes perceptible on drying the leaves or submitting them to cold by the evaporation of ethyl chloride. Exposure to the vapour of chloroform or ether acts in the same way. The odour resembles that given by *Melilotis officinalis* under the same conditions (Abstr., 1910, 63) and is probably due to the same substance.

W. O. W.

**Sensitiveness of Lupins towards Lime. Behaviour of some Other Plants Towards Alkaline and Acid Media.** REODORE PFEIFFER and E. BLANCK (*Bied. Zentr.*, 1911, 40, 394—401; from *Mitt. landw. Inst. Univ. Breslau*, 6, 273).—The results of past



experiments with *Lupinus luteus* showed that 0.1% of calcium carbonate was without appreciable effect, whilst the yield was reduced by 0.3% and still more by 0.6%. The results with calcium sulphate were conflicting, small amounts being more injurious than corresponding amounts of calcium carbonate; whilst with the larger amounts the results were reversed. Calcium phosphate also proved to be injurious, probably in part owing to the amount of phosphoric acid being excessive. With calcium nitrate the injury was also greater than with carbonate.

The conclusion is drawn that lupins are especially sensitive towards alkali, and that the injurious action of calcium salts is in part due to neutralisation of the root acids. The acidity of lupin roots, which enables the plants to thrive in certain soils better than many other plants, cannot be checked without injury to the plant.

Potatoes and beet were not affected by the amounts of alkali which are injurious to lupins.

N. H. J. M.

**Philippine Firewood.** ALVIN J. COX (*Philippine J. Sci.*, 1911, 6, 1—22).—The chief woods used in the Philippines as fuel are the *Rhizophoraceae*, composing the thick mangrove swamps of the coast.

Wood dried at 103—105° will absorb from the air an amount of moisture somewhat less than that which the air-dried wood will retain of the original moisture of the green stick; the best seasoned wood retains 12.5—13% of moisture, calculated on the weight of the dry wood, which is the only constant basis on which to compute the percentage of moisture and ash. Tables are given of the determination of the calorific values of some Philippine woods and barks, of analyses of wood ash, of the determination of the specific gravities of some Philippine woods, and of the approximate fuel value of North American and Philippine firewoods. The available heating value of the combustible matter of wood, that is, wood—(water + ash), is practically constant, and is equal to 4418 calories. From this number the available heating value of a wood, of known moisture and ash content, is given by the expression,  $4418 \times (100 - \% \text{ water} - \% \text{ ash}) / 100 - 6 \times \% \text{ water}$ . The percentage of moisture and of ash, and the specific gravity are the three most important factors controlling the fuel value of a wood. The volatile constituents of a mangrove ash are large, and may condense as clinker on the walls of a furnace, or glaze any surface with which they come in contact.

C. S.

**Fruit of *Solanum dulcamara*.** BENTON R. ANDERSON (*Chem. News*, 1911, 104, 2—3. Compare Wells and Reeder, *Abstr.*, 1908, i, 58).—The fruits lost 46.05% of their weight on extraction, first with alcohol and then with water. They contained (a) 31.55% of sugars in which levulose was observed; (b) 9.15% of oil having D 0.9603 and saponification equivalent 306, and yielding ricinoleic acid on hydrolysis; (c) 0.934% nitrogen; (d) 0.15% of alkaloid; (e) ash, containing the usual mineral constituents found in plants. The fruits also contained citric, tartaric, and acetic acids; the last probably as the result of fermentation.

T. A. H.

**The Influence of Light on the Composition of the Sugar-Beet.** **FRIEDRICH STROHMER, HERMANN BRIEM, and OTTOKAR FALLADA** (*Chem. Zentr.*, 1911, i, 1065—1067; from *Österr.-ung. Zeitsch. Zuckerind.*, 40, 11—28).—Comparative experiments on the growth of plants from the same seeds and at the same place, under as nearly comparable conditions as possible, were carried out, one portion being grown in the light, and the other under the shade of trees. With insufficient light, the leaves develop at the expense of the roots, which contain a smaller percentage of dried substance, this being accounted for mainly (74%) by the diminished sugar production. The content in nitrogenous substances was, on the other hand, higher in the roots of the plants grown in the shade. These contained a greater proportion of non-protein nitrogenous substances. The difference in the proportion of protein to non-protein nitrogen was specially marked in the leaves. The leaves of the shaded plants contained also appreciably larger quantities of oxalic acid. Tables are given showing the composition of the ash. S. B. S.

**Occurrence of Starch in Sugar-Beet Roots.** **JAVOSLAW PEKLO** (*Bied. Zentr.*, 1911, 40, 386—387; from *Österr.-ung. Zeitsch. Zuckerind. Landw.*, 38, Pt. 2).—The condensation of soluble carbohydrates to starch in the cells of sugar-beet is not merely a chemical process, but is connected with the presence of leucoplasts in the cells. Starch production can be readily noticed in roots with high percentages of sugar. N. H. J. M.

**Discrepancy between the Results Obtained by Manuring, etc., in Pots and in the Field.** **LIONEL COHEN** (*Proc. Roy. Soc. N.S. Wales*, 1909, 43, 117—122).—Divergences between the results of pot and field experiments are probably mainly due to the more variable amounts of water present in field experiments, and consequently varying concentration of soil solutions.

It is suggested that the wilting of plants observed by Sachs in clay soils containing 12% of water was due to excessive concentration of the dissolved salts. Tobacco plants in sandy soil remained turgid, when only 1.5% of water was present. N. H. J. M.

**Absorption of Ammonia from the Atmosphere.** **ALFRED D. HALL and NORMAN H. J. MILLER** (*J. Agric. Sci.*, 1911, 4, 56—68. Compare Bineau, *Ann. Chim. Phys.* 1854, [iii], 42, 428; Müller, *J. pr. Chem.*, 1866, 96, 339; Heinrich, *Abstr.*, 1882, 789; *Kellner. Landw. Jahrb.*, 1886, 15, 701).—Monthly estimations, for two years, of the amounts of atmospheric ammonia absorbed by dilute sulphuric acid in dishes 26.5 cm. in diameter.

The highest results were obtained with dishes kept at a height of about 115 cm. above the ground in front of the Rothamsted laboratory, near the outside of the town, the nitrogen absorbed amounting to 1.48 lb. per acre per annum. In dishes in the same situation, but only 5 cm. above the ground, the amount absorbed was only 0.85 lb.

Dishes placed in the experimental grass plots showed somewhat

higher results in the upper dish (0.78 lb.) than in the lower one (0.70 lb.). In the experimental wheat field the absorption in the upper dishes was 1.14 lb., and in the lower dishes 1.53 lb. The higher results obtained in the wheat field as compared with the grass plots is mainly due to considerable amounts of ammonia given off by the soil for some weeks following the application of ammonium salts to some of the wheat plots. In April, 1909, the absorption in the upper and lower dishes in the wheat field was 0.29 and 0.61 lb. respectively. During the ten months not affected by the manures, the average absorption in the wheat field was higher in the upper than in the lower dishes.

N. H. J. M.

**Action of Alumina and Silicic Acid on the Utilisation of the Phosphoric Acid in Soils by Plants.** THEODOR PREIFFER and E. BLANCK (*Bied. Zentr.*, 1911, 40, 381—383; from *Mitt. landw. Inst. Univ. Breslau*, 6, 315).—Pot experiments in which lupins were grown in sand, manured with potassium phosphate, alone and in conjunction with alumina and gelatinous silica. Some of the pots were subjected to the action of cold and heat respectively, and some received calcium chloride in addition to the other substances.

The results failed to give indications of the production of adsorption compounds. Addition of alumina and gelatinous silicic acid merely gives rise to the chemical combination of the phosphoric acid. It is, however, possible that under other conditions—omission of silica and the employment of less alumina in relation to the phosphoric acid—different indications might be obtained.

N. H. J. M.

**Utilisation of Sewage Waters in Agriculture.** ACHILLE MÜNTZ and E. LAINÉ (*Compt. rend.*, 1911, 152, 1814—1818. Compare this vol., ii, 421; Petit, *ibid.*, ii, 649).—The sewage of Paris does not lose phosphates during the treatment by bacterial beds, but as a fertilising material it is deficient in these salts, and, consequently, to obtain the best results in agriculture, phosphates must be added.

W. O. W.

**Importance of Phonolite as Potassium Manure.** THEODOR PREIFFER, E. BLANCK, and M. FLÜGEL (*Bied. Zentr.*, 1911, 40, 375—380; from *Mitt. landw. Inst. Univ. Breslau*, 6, 233).—The results of pot experiments in which oats, grown in sand and a mixture of sand and loam, were manured with phonolite (potassium silicate) showed that the manure is only utilised to a slight extent. Similar results were obtained when calcium nitrate and "humus silicate" respectively were applied along with the phonolite.

N. H. J. M.

**Action of Carbon Dioxide on Bordeaux Mixture.** CONRAD T. GIMINGHAM (*J. Agric. Sci.*, 1911, 4, 69—75. Compare Pickering, *Trans.*, 1907, 91, 1988).—The conclusion is drawn that the fungicidal action of Bordeaux mixture cannot be due to copper sulphate liberated by atmospheric carbon dioxide, and that only minute amounts of copper carbonate, if any at all, are likely to be dissolved in the rain or

dew on the surfaces of the leaves. Probably the actual contact between the fungus and the particles of the insoluble copper compound is the chief means by which further growth is prevented.

N. H. J. M.

## Analytical Chemistry.

**Tests for Purity, and the Washing of Precipitates in Relation to Adsorption.** K. SCHERINGA (*Pharm. Weekblad*, 1911, 48, 674—675. Compare *Chem. Weekblad*, 1911, 8, 11).—From his experimental results the author draws the conclusions: (1) Tests for purity are rendered more delicate by washing a substance insoluble in water with a salt solution. (2) The washing of precipitates can often be accelerated or improved by employing a solution of a volatile organic or inorganic substance instead of water. (3) The method is applicable to washing photographs. (4) In cases of acute poisoning, the stomach should be washed out with a salt solution. A. J. W.

**Modified Colorimeter and Some Tests of its Accuracy.** EDWARD D. CAMPELL and WILLIAM B. HURLEY (*J. Amer. Chem. Soc.*, 1911, 33, 1112—1115).—A simple form of colorimeter is described in which the solution to be examined is contained in one of a pair of cylindrical tubes, the second containing the standard solution, the level of which can be raised or lowered by means of a glass plunger working in an attached reservoir. The light passing upwards through the tubes impinges on two mirrors at an angle of  $45^\circ$  to the vertical. One of these mirrors is cut vertically and cemented in such a position as to reflect one half of the circular field of light coming through one of the tubes. One half of the circular beam from the second tube and mirror is cut off by the first mirror, and in this way two juxtaposed images, separated by a vertical dividing line, are to be seen through the observing tube. This is lined with black felt, and is provided with a diaphragm which allows only the light from the bottoms of the two comparison tubes to reach the eye-piece.

Data showing the efficiency of the apparatus are recorded for titanium solutions coloured yellow by the action of hydrogen peroxide.

H. M. D.

**Determination of the Constants of the Differential Blood-gas Apparatus.** JOSEPH BARCROFT and H. L. HIGGINS (*J. Physiol.*, 1911, 42, 512—518).—Important data are given for the use of the instrument.

W. D. H.

**Estimation of Chlorides in [Commercial] Bromides.** H. RABE (*Pharm. Zeit.*, 1911, 56, 505).—One gram of the bromide to be tested is dissolved in 100 c.c. of water and titrated with  $N/10$ -silver nitrate. The amount of chloride is then found from the equation  $y = mx + b$ , in

which  $x$  represents the number of c.c. of silver used, whereas  $m$  and  $b$  are constants. For ammonium bromide,  $m=20/17$  and  $b=120$ ; for potassium bromide,  $m=2$  and  $b=168$ ; for sodium bromide,  $m=50/31$  and  $b=4850/37$ .

L. DE R.

**Phenomenon of Occlusion in Precipitates of Barium Sulphate, and its Relation to the Exact Estimation of Sulphates.** JOHN JOHNSTON and L. H. ADAMS (*J. Amer. Chem. Soc.*, 1911, 33, 829—845).—It has been pointed out by Allen and Johnston (*Abstr.*, 1910, ii, 650) that in the estimation of sulphates by the usual method an error of 1% or even more may be occasioned by the occlusion of foreign substances, especially alkali sulphates, by the precipitated barium sulphate.

It has now been found that the amount of impurity occluded depends on the concentration of the salts in the original solution and on the fineness of the precipitate, the latter factor being controlled by the rate of precipitation, the solubility of the barium sulphate in the supernatant liquid, and the interval which is allowed to elapse between precipitation and filtration. It is shown that the occlusion is probably a phenomenon of absorption at the surface of the grains of the precipitate.

The following method, based on these results, is recommended for the exact estimation of sulphates. To 30 c.c. of the solution, which should be of such a concentration as to yield a precipitate weighing about 2 grams, 50 c.c. of concentrated hydrochloric acid are added. The mixture is heated until it boils, and a 10% solution of barium chloride is added drop by drop until precipitation is complete; the latter operation should take about four minutes. The whole is evaporated to dryness on the water-bath, and the residue treated with hot water; the barium sulphate is collected, washed until free from chlorides, ignited carefully in such a way as to obviate reduction, and heated with the bunsen burner until of constant weight. The correction to be applied is determined by making a solution of alkali sulphate of nearly the same composition as the solution under examination, and estimating the sulphate in it in exactly the same manner. The difference between the calculated amount of barium sulphate and that actually found is the correction required.

This method is easier and more rapid than Allen and Johnston's (*loc. cit.*), but is not so generally applicable. When, however, the approximate composition of the solution containing the sulphate is known, the new method will give results within  $\pm 0.05\%$  of the total sulphate present.

E. G.

**Analysis of Nitrous Oxide.** WARREN R. SMITH and E. D. LEMAN (*J. Amer. Chem. Soc.*, 1911, 33, 1116—1117).—The composition of the gas drawn off from cylinders containing liquid nitrous oxide depends on the rate at which the gas is removed, the length of time elapsing between the withdrawal of samples and various other factors. To avoid the uncertainties which are thus caused by the greater volatility of the admixed nitrogen and oxygen, the authors recommend

be expedient of inverting the cylinder, and drawing a sample from the bottom of the liquid. This is shown to give a fair sample.

H. M. D.

**Detection of Nitrates with Diphenylamine.** HUBERT CARON *Ann. Chim. anal.*, 1911, 16, 211—215).—Minute traces of nitrates may be detected, as is well known, by the diphenylamine test. According to the author the reagent is best prepared by dissolving 1 mg. of diphenylamine in 100 c.c. of pure sulphuric acid; 2½ volumes of this are then added to 1 vol. of the nitrate solution. The ring test does not seem to be more delicate. If, however, the reagent is intended for a colorimetric estimation, and when the liquid under examination also contains chlorides, it is best prepared by dissolving 1 mg. of diphenylamine in 100 c.c. of sulphuric acid mixed with 40 c.c. of water and 2 or 3 c.c. of *N*/10-hydrochloric acid; 5 c.c. of this are then added to ½ c.c. of the nitrate solution, and the mixture is gently heated. Among the substances which interfere with the reaction may be mentioned methyl and ethyl alcohol, glycerol, ethyl ether, acetone, and hydrocarbons.

L. DE K.

**Estimation of Nitric Acid.** GYSBERT ROMYN (*Pharm. Weekblad.*, 1911, 48, 753—757; *Zeitsch. anal. Chem.*, 1911, 50, 566—570).—One hundred grams of ammonium sulphate and 100 c.c. of ammonia (D 0.96) are dissolved and made up to 500 c.c. Five c.c. of this reagent are placed in a 100 c.c. flask, which is then filled with the nitrate solution to be tested; this should be free from iron and not contain more than 0.4 gram of nitrogen pentoxide per litre. The liquid is transferred to a dry flask, 0.2 gram of zinc dust mixture is added, and after closing the flask the contents are well shaken; after about five minutes, 95% of the nitrate is converted into nitrite. (The zinc mixture is prepared by intimately mixing zinc dust, "extra fine," with an equal weight of kieselguhr.) After pouring through a dry filter, 50 c.c. of the clear filtrate are placed in a dry stoppered flask, and 10 c.c. of *N*/10-permanganate followed by 5 c.c. of dilute sulphuric acid are added. After waiting for half an hour, 5 c.c. of 3% potassium iodide solution are added, and the iodine liberated is titrated with *N*/10-thiosulphate.

L. DE K.

**Detection and Estimation of Nitric and Nitrous Acid in Waters.** J. TILLMANN and W. SUTTHOFF (*Zeitsch. anal. Chem.*, 1911, 50, 473—493).—A lengthy article on the detection and colorimetric estimation of nitric and nitrous acid, or both, in waters. The following are the most important points. For the detection of nitric acid + nitrous acid, the following reagent is used: 0.085 gram of diphenylamine is covered in a 500 c.c. flask with 190 c.c. of dilute sulphuric acid (1 : 3), and sufficient strong acid is then added to heat the liquid and cause the diphenylamine to dissolve; more sulphuric acid is then added nearly up to the mark, and when cold the volume is exactly made up. When testing a water, 100 c.c. are mixed with 5 c.c. of brine, so as to promote the reaction, 1 c.c. of the water is shaken with a delicate pipette, and 4 c.c. of the reagent are added. The

blue coloration is observed and matched after one hour. It gradually begins to fade and discolour after that time.

For the detection and colorimetric estimation of nitrous acid alone, a slightly different reagent is used [0.06 gram of dimethylamine, 325 c.c. of dilute sulphuric acid (1:3), sulphuric acid up to 500 c.c.]. Five c.c. of the water, to which no brine need be added, are mixed with 5 c.c. of the reagent, and the mixture is at once cooled. The blue colour due to nitrous acid alone reaches its maximum in about twenty minutes, and then soon fades. If it is desired to make a direct estimation of the nitric acid also, the water may be freed from nitrite by boiling, for instance, with a little ammonium chloride.

L. DE K.

**Titration of Phosphates.** WILHELM STRECKER and PAUL SCHIFFER (*Zeitsch. anal. Chem.*, 1911, 50, 495—499).—Aliquot portions of a solution of sodium hydrogen phosphate were tested (1) by evaporation and heating and weighing as sodium pyrophosphate, (2) by weighing as phosphomolybdic anhydride according to Woy's method, (3) by titration with uranyl acetate, and (4) by precipitation with standard silver nitrate in acetic acid solution and determining the excess of silver by Volhard's process, a method proposed originally by Perrot in 1881, but since taken up by Holleman and others.

The results obtained by these four methods were quite concordant.

L. DE K.

**Volumetric Estimation of Phosphoric Acid.** J. ROSIN (*J. Amer. Chem. Soc.*, 1911, 33, 1099—1104).—The reaction between silver nitrate and disodium hydrogen phosphate in aqueous solution corresponds with the equation:  $3\text{Na}_2\text{HPO}_4 + 6\text{AgNO}_3 = 2\text{Ag}_3\text{PO}_4 + 6\text{NaNO}_3 + \text{H}_3\text{PO}_4$ . The filtered solution contains from 35 to 38% of the original phosphoric acid; this is greater than the 33.3% required by the equation, but the excess is probably due to the solvent action of the liberated phosphoric acid on the silver phosphate. The observed reaction is made the basis of a volumetric method for the estimation of phosphoric acid. The phosphoric acid solution is made neutral to phenolphthalein by addition of sodium hydroxide, an excess of 0.1N-silver nitrate being then added, and the mixture well shaken. Zinc oxide is then added little by little until the acid reaction towards litmus paper disappears. The solution is now made up to a known volume with water, the precipitate allowed to settle, and the solution filtered. The excess of silver is then determined in an aliquot portion of the filtrate by Volhard's method. The method yields satisfactory results if the excess of silver nitrate added does not fall below 30% of that which is required for precipitation of the phosphoric acid, and if, after addition of the zinc oxide, the mixture is not left too long before filtering. The method can be used in presence of sulphates, nitrates, chlorides, and calcium, but cannot be used for the estimation of the total phosphoric acid in presence of more than traces of iron and aluminium.

The reaction between zinc phosphate and silver nitrate, on which the process depends, is also found in the case of other insoluble

phosphates. In general, those phosphates which are soluble in acetic acid are reacted on in this way by silver nitrate, while those which are insoluble in acetic acid are inactive.

H. M. D.

#### Estimation of Arsenic and of Iron Salts in Mineral Waters.

F. AGENO and N. GUICCIARDINI (*Gazzetta*, 1911, 41, i, 473—478).—For the analysis of the water of Roncegno (compare Abstr., 1910, ii, 222), which contains arsenites, arsenates, ferrous and ferric salts, and organic matter, the following methods were employed.

Titration in acid solution with permanganate gives the amount of the latter corresponding with the ferrous salts, arsenites, and organic substances. Separate determinations are made of the total iron and of the total arsenic. The latter is estimated by the method of Andrews and Farr (Abstr., 1909, ii, 437), the arsenic being precipitated in the metallic state by adding 2—5 volumes of a solution containing 10 grams of crystalline stannous chloride and 40 grams of tartaric acid per litre of 40% hydrochloric acid; the arsenic is then dissolved in excess of a standard iodine solution containing sodium hydrogen carbonate,  $As + 5I + 7NaHCO_3 = Na_2HASO_4 + 5NaI + 7CO_2 + 3H_2O$ , the excess of iodine being determined by titration with arsenious anhydride. For the separate estimation of the arsenites, the iron salts are eliminated by precipitation with boiling sodium or potassium hydroxide and carbonate; the filtered liquid is treated with carbon dioxide to convert the hydroxides into carbonates, and titrated with iodine solution. The ferrous salts are estimated after elimination of the sulphuric acid under conditions which do not admit of the ferrous salts being oxidised, thus: the sulphuric acid is precipitated in solution lightly acidified with hydrochloric acid in a fairly large flask fitted with a three-holed stopper, through which pass the end of the barium chloride burette and a carbon dioxide delivery tube dipping below the surface of the liquid, the third hole allowing the gas to escape; the ferric and ferrous salts are then separated by the method given by Fresenius. The amounts of the separate constituents can then be calculated.

T. H. P.

**Sodium Thiosulphate as the Standard Substance in Alkalimetry.** WALTER FELD (*Zeitsch. angew. Chem.*, 1911, 24, 1161—1163).—With excess of mercuric chloride, sodium thiosulphate reacts according to the equation:  $Na_2S_2O_3 + 2HgCl_2 + H_2O = Hg_2Cl_2 + Na_2SO_4 + 2HCl + S$ , 2 mols. of acid being liberated for every molecule of sodium thiosulphate (compare this vol., ii, 289). Since sodium thiosulphate can be obtained in a very pure state from Merck, the author recommends that the above reaction should be used to standardise solutions of alkali, the acid liberated being titrated by the alkali to be standardised. For the estimation, a cold saturated solution of mercuric chloride and a 4*N*-solution of ammonium chloride are used. The thiosulphate solution is added to excess of the mercuric chloride solution, and when the reaction is complete, either in the cold or on warming, an excess of ammonium chloride solution is added, and then the acid titrated with alkali, using methyl-orange as indicator. The ammonium chloride is necessary to prevent yellow mercuric oxide



being precipitated by the action of the alkali on the excess of mercuric chloride; it must never be added before the reaction between the thiosulphate and mercuric chloride is complete, otherwise it hinders the reaction.

Excess of mercuric chloride is necessary, otherwise mercuric sulphide is formed according to the equation:  $\text{Na}_2\text{S}_2\text{O}_3 + \text{HgCl}_2 + \text{H}_2\text{O} = \text{HgS} + \text{Na}_2\text{SO}_4 + 2\text{HCl}$ , and masks the colour change of the indicator.

The author finds that Merck's sodium thiosulphate (solid) keeps well, at least for a year, in a corked bottle. T. S. P.

**Rapid Estimation of Silver and Cadmium by means of the Gauze Cathode and Stationary Anode.** RAYMOND C. BENNETT and WILLIAM H. ROSS (*J. Amer. Chem. Soc.*, 1911, 33, 1106—1112).—Experiments have been made to determine the best conditions for the electro-deposition of silver and cadmium. In both cases the best results are obtained with cyanide solutions to which alkali hydroxide has been added.

The deposition of silver, in quantities from 0.15 to 0.3 gram, can be carried out with currents up to 5 amperes, and the strength of the current appears to have little influence on the character of the deposit. The rate of deposition diminishes as the concentration of the potassium cyanide is increased, but the amount of silver which can be deposited in an adherent form may be correspondingly increased. For quantities of silver weighing less than 0.3 gram, the most satisfactory results were obtained when about 8 grams of potassium cyanide were added to 60 c.c. of solution.

The concentration of cyanide has much less effect on the character of the deposit in the case of cadmium. When deposited from solutions containing no hydroxide, the solution became coloured, and slightly higher results were obtained. This effect is not observed, however, when potassium hydroxide is added to the solutions. The addition of 2 grams of potassium hydroxide and 6 grams of potassium cyanide to 75 c.c. of solution is recommended. H. M. D.

**Method for the Separation of the Metals of the Ammonium Carbonate Group (Calcium, Barium, and Strontium).** ERICH BIRNBRÄUER (*Chem. Zeit.*, 1911, 35, 755).—The precipitate of mixed carbonates is dissolved in dilute nitric acid, and the solution evaporated to dryness on the water-bath. Calcium nitrate, if present, is extracted from the residue by repeated treatment with a 1:1 mixture of alcohol and ether; the solution so obtained is evaporated to dryness, the calcium nitrate dissolved in water, and the calcium precipitated as oxalate.

The residue of barium and strontium nitrates is dissolved in a small quantity of hot water, acetic acid and ammonium acetate or ammonia added to the solution, which should smell of acetic acid, and the barium precipitated as chromate by the addition of ammonium dichromate and boiling. Strontium is precipitated as sulphate from the filtrate by the addition of 1:2 ammonium sulphate solution. T. S. P.

**The Volumetric Estimation of Lead Peroxide.** JULIUS F. SACHSE (*Chem. Zeit.*, 1911, 35, 731).—The author has observed that

lead peroxide is somewhat soluble in nitric acid, and this causes errors in the estimation of the lead peroxide-content according to Lux's method (Abstr., 1880, 585). The error is avoided if the oxalic acid is added before the treatment with nitric acid. Before the titration with permanganate, the lead may be precipitated as sulphate with sulphuric acid; it is not necessary to filter off the lead sulphate before titrating.

Forestier's method (*Zeitsch. angew. Chem.*, 1898, 11, 176) is inaccurate.  
T. S. P.

**Galvanic Estimation of Copper in Preserves.** K. LAKUS (*Zeitsch. Nahr. Genussm.*, 1911, 21, 662—664).—Around an amalgamated zinc rod, 4 to 5 cm. in length, is twisted in two or three windings a copper wire. The solution to be tested (obtained by treating the ash with sulphuric acid) is placed into a perfectly clean and polished platinum dish. The about 5 cm. long end of the wire is laid over the edge of the dish in such a manner that the rod dips, in the middle of the dish, about 1 cm. deep into the liquid. As in this way the zinc does not come into direct contact with the platinum, and owing to the amalgamation, no hydrogen is evolved, and the copper forms a firmly adhering deposit of a normal colour.  
L. DE K.

**Analysis of Materials Containing Copper, Nickel, and Cobalt.** HARALD PEDERSON (*Metallurgie*, 1911, 8, 335).—The finely powdered material is attacked by fuming nitric acid, and is then twice evaporated with sulphuric acid. The iron is twice precipitated from the solution by ammonia, and after acidifying the filtrate with sulphuric acid, the copper is estimated electrolytically. Only traces of nickel and cobalt are deposited on the cathode. The solution is then rendered ammoniacal, and nickel and cobalt are deposited electrolytically. The deposit is dissolved in hot concentrated nitric acid, evaporated with addition of hydrochloric acid to remove nitric acid, diluted, and mixed with a 1% alcoholic solution of dimethylglyoxime, a small excess of ammonia being then added. The nickel precipitate is collected on a Gooch filter, washed with hot water, and dried at 10—120°.  
C. H. D.

**Qualitative Detection of Mercury by Klein's Method.** WILLIAM C. MOORE (*J. Amer. Chem. Soc.*, 1911, 33, 1117—1119).—The use of a solution containing potassium iodide, sodium hydroxide, and ammonia is recommended for the detection of mercury. By a comparison test with a standard solution of mercury, it is possible to estimate roughly the quantity of mercury present in a given solution.  
H. M. D.

**Detection of Mercury in Urine.** ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1911, 72, 387—401. Compare Hofmeister, *Arch. exp. Path. Pharm.*, 1884, 25, 225; Siebert, Abstr., 1910, ii, 656).—The urine is made distinctly acid by the addition of hydrochloric acid, and is evaporated first over the free flame and finally on the water-bath until salt begins to separate. The addition of 2 c.c. of

25% hydrochloric acid to each 500 c.c. of urine is usually sufficient. The mixture is then oxidised with hydrochloric and chloric acids and evaporated, and the residue extracted with alcohol. The alcoholic extract is evaporated, again oxidised, evaporated, and extracted with 40 c.c. of absolute alcohol; 60 c.c. of ether are added to precipitate most of the salts and the whole filtered. The alcoholic ethereal solution is evaporated, and the residue extracted by 10 c.c. of water by strongly shaking. After filtration through a stout filter-paper, five drops of a solution of stannous chloride and hydrochloric acid are added. If a turbidity or precipitate is formed, more hydrochloric acid is added. If the reaction is negative, the first alcoholic residue can be extracted with aqueous hydrochloric acid, filtered, evaporated, oxidised, and the same test again applied.

J. J. S.

**Colorimetric Estimation of Mercury in Urine.** ALFRED HEINZELMANN (*Chem. Zeit.*, 1911, 35, 721—722).—The method given by Schumacher and Jung (*Abstr.*, 1903, ii, 44) for the estimation of mercury in urine is unsatisfactory. Errors are caused by the chlorine liberated when potassium chlorate is added to accelerate the solution of the zinc amalgam, and by the precipitating effect of the hydrochloric acid present on the colloidal mercuric sulphide. The following method is recommended by the author: 500 c.c. of urine are heated in a litre flask with 5 grams of potassium chlorate and 50 c.c. of hydrochloric acid ( $D = 1.12$ ). When the mixture has become limpid and light yellow in colour, it is cooled to  $70^{\circ}$ , 10 grams of pure rasped zinc added, and left overnight. The urine is then poured off from the zinc, which is washed several times with water and then dissolved in 50 c.c. of hydrochloric acid ( $D = 1.18$ ). Twenty grams of potassium acetate are added, the solution transferred to a Hehner cylinder and made up to 90 c.c. with water, and then to 100 c.c. with hydrogen sulphide water. The colour is then compared with that of a standard prepared at the same time from mercuric chloride. The comparison of colour should be made after about five minutes; the solutions obtained after the addition of the hydrogen sulphide water are stable only for about twenty minutes.

T. S. P.

**Analysis of Aluminium and its Alloys.** GEORG KLEIST (*Chem. Zeit.*, 1911, 73, 668—669).—The silicon in "pure" aluminium is determined as by Smith (*Chem. Zeit. Repert.*, 1911, 45, 188), but without special addition of sulphuric acid. For iron, 2—5 grams are heated in an Erlenmeyer flask with 100 c.c. of dilute sodium hydroxide until dissolved. The solution is strongly acidified with sulphuric acid, filtered, diluted to about 600 c.c., and titrated with permanganate. For copper and tin, the filtrate from the estimation of silicon is saturated with hydrogen sulphide, filtered, and the precipitate washed with cold water, ignited, and weighed as cupric and stannic oxides. If tin is present, as shown by insolubility in nitric acid, it is estimated as described later. The filtrate is concentrated to about 100 c.c., the iron thrown out with sodium hydroxide, then boiled, and filtered. Traces of zinc are precipitated from the filtrate by hydrogen sulphide, collected, ignited, and weighed as zinc oxide. In the case of alloys, the silicon and

Iron are determined in like manner, and the copper and tin in the filtrate are precipitated together as before. The tin is separately found by heating 1—2 grams of the alloy in an Erlenmeyer flask, provided with a bored rubber cork, with 150 c.c. of hydrochloric acid (D 1.19) until dissolved. The boiling liquid is titrated with ferric chloride solution, which has stood over pure tin, the end being marked by a yellow tinge. Otherwise, the weighed precipitate of cupric and stannic oxides may be dissolved in nitric acid, filtered, and the copper found by electrolysis or titration with potassium cyanide may be resorted to. The filtrate from the copper and tin is concentrated to 100 c.c., ammonia added, and just enough sulphuric acid to redissolve the alumina. After dilution to 400—500 c.c., hydrogen sulphide is passed in to saturation, and the zinc sulphide collected and washed with very dilute sulphuric acid containing some ammonium sulphate and hydrogen sulphide. The precipitate is dissolved from the filter with hot dilute hydrochloric acid, made slightly ammoniacal, boiled, and filtered. The filtrate is very slightly acidified with sulphuric acid, and the zinc re-precipitated by hydrogen sulphide.

J. D. K.

**Separation of Aluminium and Glucinum.** M. WUNDER and (Mlle.) NINA CHÉLADZÉ (*Ann. Chim. anal.*, 1911, 16, 205—209).—The separation of glucinum from aluminium by taking advantage of the solubility of glucinum hydroxide in concentrated ammonium carbonate gives utterly untrustworthy results. The separation by means of potassium or sodium hydroxide which dissolves both hydroxides, but deposits the glucinum hydroxide only when the solution is sufficiently diluted and boiled for an hour (taking care to replace the water evaporated), seems, however, quite satisfactory. The aluminium is then recovered from the filtrate by acidifying with hydrochloric acid and reprecipitating with ammonia.

L. DE K.

**Estimation of Chromium in Chrome Iron Ore.** OTTO NYDEGGER (*Zeitsch. angew. Chem.*, 1911, 24, 1163—1164).—0.5 Gram of the powdered ore (not necessarily finely powdered) is heated with 5 grams of borax fusion mixture (made by fusing two parts of anhydrous sodium carbonate with one part of borax glass) in a platinum crucible over a good bunsen flame for one to two hours, or until all the ore has been taken up. The fused mass is dissolved from the cooled crucible with 300—400 c.c. of water containing 4 c.c. of concentrated sulphuric acid, and any chromium remaining unoxidised is transformed into chromate by the addition of 0.2 gram of potassium persulphate, which at the same time precipitates any manganese present as peroxide. The excess of persulphate is destroyed by boiling for thirty to forty minutes, the solution filtered from the manganese peroxide, and the filtrate titrated with standard ferrous ammonium sulphate solution, using potassium ferricyanide as indicator.

T. S. P.

**A Reaction for Uranium Salts.** J. A. SIEMSEN (*Chem. Zeit.*, 1911, 35, 742).—A weighed quantity of the uranium salt is dissolved in water and a 10% solution of ethylenediamine added drop by drop

until a precipitate no longer forms (compare this vol., ii, 230). The precipitate, which is insoluble in water and the usual organic solvents, is washed with water, collected, dried, and ignited to the oxide,  $U_3O_8$ . The results are quantitative.

A solution of ethylenediamine more dilute than 10% should not be used, otherwise a gelatinous precipitate is formed. The precipitate is insoluble in excess of the precipitant (*loc. cit.*), but soluble in excess of the uranium salt.

T. S. P.

**Behaviour of Zirconium Oxide Towards Hydrofluoric Acid.** EDGAR WEDEKIND (*Ber.*, 1911, 44, 1753—1755. Compare Weiss and Neumann, *Abstr.*, 1910, ii, 217).—When zirconium silicides, or zirconium metal containing silicon, or mixtures of the oxides of zirconium and silicon, are treated with a mixture of sulphuric and hydrofluoric acids to remove the silicon, some of the zirconium is often volatilised. This can be prevented by the addition of sufficient sulphuric acid, the zirconium material being treated with a mixture of twenty times its amount of concentrated sulphuric acid with forty-five times its amount of hydrofluoric acid; the zirconium is weighed as oxide,  $ZrO_2$ , formed from the sulphate by ignition.

Attempts to determine the combined silica in zirconium silicate (hyacinth) by the above method were unsuccessful.

T. S. P.

**Quantitative Chemical Analysis of Mixtures by means of Differences in Density.** MICHAEL A. RAKUSIN (*Ber.*, 1911, 44, 1676).—The author points out that the centrifugal method used by Friedenthal (this vol., ii, 555), even with 3000 revolutions per minute, causes considerable alterations in the optical and other properties of the earth-oils investigated. In one case the density diminished by 0.002—0.003, whilst the carbonisation constant rose about 30%.

T. S. P.

**Estimation of Camphor in Smokeless Powders.** MARQUETTE (*Ann. Chim. anal.*, 1911, 16, 209—210).—Ten grams of the powder are extracted with ether in a Soxhlet tube for ten hours. The ether is poured into a beaker of 65—70 mm. in diameter and 35—40 mm. in height, which is then placed in a desiccator over sulphuric acid, and when the volume of the ether is reduced to a few c.c., the beaker is covered with a glass disk and rapidly weighed. The beaker is replaced in the desiccator, and the weighings are repeated, say, every ten minutes. Finally the camphor is expelled by heating at 30—35° and another weighing is taken.

L. DE K.

**Estimation of Glycerol in Fats and Soaps.** ADOLF BEYTHIES, H. HEMPEL, P. SIMMICH, W. SCHWERDT and C. WIESMANN (*Zeitsch. Nahr. Genussm.*, 1911, 21, 673—675).—In the absence of soluble fatty acids (butyric, for instance), the original process of Benedikt and Zsigmondy (oxidation with alkaline permanganate and estimation of the oxalic acid formed) gives very satisfactory results.

In the presence of compounds acted on by permanganate, the acetic process should be employed. The dichromate process much used in

soap works also gives good results provided the leys have been properly defecated with basic lead acetate.

L. DE K.

**Determination of the Rotatory Power of Some Organic Substances in Presence of Lead Reagents; Inconvenience of Distilled Water Containing Carbon Dioxide.** HENRI PELLET (*Ann. Chim. anal.*, 1911, 16, 215—218).—Contrary to Sellier's statement that a solution of glutamine yields a gradually increasing precipitate with basic lead acetate, the author states that with pure glutamine no precipitate is obtained provided the water is absolutely free from carbon dioxide. No trouble is experienced in the polarisation.

Glutamic acid, asparagine, aspartic acid, raffinose, invert sugar, dextrose, and levulose are also unaffected by basic lead acetate.

L. DE K.

**Estimation of Gum in Syrups.** XAVIER ROCQUES and G. SELLIER (*Ann. Chim. anal.*, 1911, 16, 218—220).—A process recently published by Chauvin (*Mon. Sci.*, 1911, May), but which has been already employed by one of the authors for some years.

Twenty-five grams of the syrup are mixed with 80 c.c. of alcohol (90° French), slowly at first, 2 c.c. of a saturated alcoholic solution of lead acetate are added, and the precipitate is allowed to settle for twenty minutes. It is then collected on a tared filter, and washed with alcohol (75°). After drying, the precipitate is weighed, and, after allowing for the lead oxide it contains (calcination with nitric acid), the result equals pure gum, which multiplied by 1.18 represents ordinary gum arabic.

If it is desired to know the weight of gum per litre of syrup, 20 c.c. are diluted with 10 c.c. of water, 2 c.c. of alcoholic lead acetate are added, and then 90 c.c. of alcohol (95°). The precipitate is then treated as before.

L. DE K.

**Estimation of Salicylic Acid in Fruit Juices.** P. VIERHOUT (*Zeitsch. Nahr. Genussm.*, 1911, 21, 664—666).—Fifty c.c. of the juice are placed in a spacious separating funnel, 15 drops of sulphuric acid are added, and the mixture shaken with 50 c.c. of light petroleum, b. p. 40—60°.

In order to destroy the thick emulsion, 25 c.c. of 96% alcohol are added, and the whole again shaken. After siphoning off the supernatant liquid into a measure, the remainder is again shaken with 50 c.c. of light petroleum, and then with 25 c.c. of alcohol. The whole of the contents of the funnel are now poured into the measure, and the liquid is made up to 200 c.c. by adding a mixture of 5 vols. of light petroleum and 2½ vols. of alcohol. The whole is shaken for a moment, and 50 c.c. of the supernatant liquid (12.5 c.c. of the sample) are pipetted off into a small flask containing a few grams of dry sodium sulphate, and, after closing the flask, the whole is allowed to remain for two hours. The solution is then filtered through a dry filter into an Erlenmeyer flask containing 50 c.c. of N/10-sodium hydroxide, the sodium sulphate is washed with a few more c.c. of the

alcohol-petroleum mixture, and the light petroleum is distilled off. The excess of alkali is then titrated with *N*/10-acid, and the percentage of salicylic acid found by an easy calculation. L. DE K.

**Iodometric Estimation of Uric Acid in Urine.** DIOSCORIDIS VITALI (*Boll. Chim. Farm.*, 1911, 50, 365—366).—The author has already described (*Abstr.*, 1899, i, 117) the reaction which Pizzorno (this vol., ii, 667) proposes to apply for the above purpose, but he did not propose it as a method of estimation, because there may well be other substances in urine which will consume iodine. R. V. S.

**Estimation of Formaldehyde by the Ammonia Process.** ADOLF BEYTHIEN, H. HEMPEL, P. SIMMICH, W. SCHWERDT, and C. WIESEMANN (*Zeitsch. Nahr. Genussm.*, 1911, 21, 671—673).—Smith's modification of the ammonia process is recommended (2 grams of ammonium chloride are dissolved in 25 c.c. of water, 2.5 c.c. of the formalin are added, and then 25 c.c. of *N*-sodium hydroxide. After remaining for half an hour in a closed flask, the excess of ammonia is titrated with *N*-acid, using rosolic acid as indicator.

Other indicators, such as cochineal and methyl-orange, are less suitable, and litmus, phenolphthalein, and Congo-red must be rejected altogether. L. DE K.

**Assay of Paraldehyde.** R. RICHTER (*Pharm. Zeit.*, 1910, 56, 536—538).—The author states that as the "D.A.-B.V." seems to insist on the presence of 4% of aldehyde in the drug paraldehyde, the density of the sample at 15° may be as low as 0.993, instead of 0.998—1.000. About one-half may pass over on distillation before the temperature of 123° is reached. When observing the solidifying point, it must be remembered that besides aldehyde, metaldehyde is also formed, which elevates the solidifying point. The amount of metaldehyde is found with fair accuracy by evaporating 10 grams of the sample at 50° and weighing the residue.

In the author's opinion the presence of aldehyde in the drug renders it less suitable for medicinal purposes, and an article as follows should be prescribed:  $D_{15} = 0.998$ —1.000, b. p. 124.7—125.2°, solidifying point 10—12°; metaldehyde to be estimated as directed. Aldehyde may be tested for by the colour given on warming at 50—60° with an equal volume of 5% potassium hydroxide. L. DE K.

**Estimation of Acetone in Animal Liquids.** H. SCOTT-WILSON (*J. Physiol.*, 1911, 42, 444—470).—A new method based on that of Marsh and Struther's mercuric cyanide process (*Trans.*, 1905, 87, 1878) is described. Urine contains some substance which, after exposure to alkali, yields on distillation with acid an additional amount of acetone. The average daily excretion of free and combined acetone in human urine is 2—4 mg. The amount runs parallel to the nitrogen. W. D. H.

**Detection and Estimation of Cyanamide in the Presence of other Fertilisers.** L. VUAFLEART (*Ann. Patisif.*, 1911, 4, 321—324).—Cyanamide may be recognised, even in the presence of other manures,

by its peculiar odour, due to the action of moisture on traces of calcium carbide. When moistened with sulphuric acid, a heavy fine powder is left, whilst organic manures (blood, for instance) leave a swollen, brown mass. Contrary to expectation, cyanamide yields all its nitrogen as ammonia by soda-lime combustion. The assay of commercial samples is as follows:

One gram of the sample is shaken in a closed vessel with 250 c.c. of water for a few hours. Of the filtrate, 100 c.c. are mixed with 20 c.c. of 5% silver nitrate solution and then 20 c.c. of ammonia. The precipitate is washed with cold water, and then re-dissolved in dilute nitric acid (1:2). The silver is then estimated by the thiocyanate method: 108 parts of silver = 14 parts of nitrogen. On an average, 87.3% of the total nitrogen exists as cyanamide. Dicyanodiamide, which is present in old samples, may be estimated jointly with cyanamide by mixing 100 c.c. of the solution (this time of double strength) with silver solution, but adding, instead of ammonia, 20 c.c. of 10% potassium hydroxide. After washing the precipitate the nitrogen is determined by the Kjeldahl process.

L. DE K.

**Analysis of Calcium Cyanamide.** ALBERT STUTZER (*Chem. Zeit.*, 1911, 35, 694).—It is pointed out that the unsatisfactory results obtained by Monnier (this vol., ii, 668) in the estimation of calcium cyanamide by precipitation as the silver salt and determination of the silver in the precipitate by means of ammonium thiocyanate, confirm the experiments of the author and Söhl (Abstr., 1910, ii, 1009) and of Caro (this vol., i, 118), who, at the same time, give an satisfactory method of analysis. Also, in contradistinction to Monnier, the author finds that the Kjeldahl method for the determination of the total nitrogen is quite satisfactory; furthermore, he does not agree with Monnier's results as to the amount of nitrogen present which has for its source the coal used in the manufacture of the calcium carbide.

T. S. P.

**A Delicate Test for Acetanilide.** G. N. WATSON (*Amer. J. Pharm.*, 1911, 83, 269—270).—By heating a mixture of acetanilide and boric acid over the bare flame until the boric acid melts, a yellow residue is obtained, having a peculiar fragrant odour resembling sweet clover or arbutus. The yellow colour is, however, also given by phenacetin. Antipyrin gives a pink colour and an odour of naphthalene. Phenacetin gives an odour characteristic of itself, but very faint. With mixtures of the three, the fragrant odour produced by the acetanilide is sufficient to give the characteristic odour, which is intensified by moistening the residue with water.

Reversely, acetanilide may, perhaps, be used as a test for boric acid.

L. DE K.

**Reactions of Pyramidone.** A. MOULIN (*Ann. Chim. anal.*, 1911, 16, 220—221).—If pyramidone in powder is treated with a drop of nitric acid, decomposition takes place with evolution of nitrous fumes, and the spot first turns yellow with a bluish-black zone, but gradually becomes a pale blue.



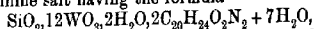
Solutions of pyrimidone are not coloured blue by nitric acid unless nitrous vapours are present. Nitrates which are easily decomposable, such as mercury or silver nitrate, also cause the coloration to appear.

L. DE K.

**Alkaloid Reactions. Arecoline.** C. REICHARD (*Pharm. Zentr.-h.*, 1911, 52, 711—716).—A large number of colour reactions given by arecoline with reagents are described. The following are the most characteristic. On adding arecoline hydrobromide to cold sulphuric acid, a colourless solution with a few minute crystals is formed. On warming, a cloudiness appears near the crystals, then spreads through the liquid, and finally disappears. Nitric acid behaves similarly. With potassium dichromate and a drop of water, a green tint is produced as the mixture dries, and becomes more pronounced on adding hydrochloric acid, but is never very intense. Ammonium molybdate behaves similarly, giving a pale blue coloration. With potassium ferrocyanide, the alkaloid gives after some hours a bluish coloration changing slowly to green, and with potassium ferricyanide a bright green with characteristic crystalline forms. The ferrocyanide residue becomes blue on adding hydrochloric acid, whilst the ferricyanide residue becomes darker green with bluish tones. These and other reactions are described in detail in the original.

T. A. H.

**The Crystalline Deposit of a Certain Fluid Extract of Cinchona Bark. The Estimation of the Quinine Alkaloids and Quinine Silicotungstate.** MAURICE JAVILLIER and B. GUÉBITHAULT (*Chem. Zentr.*, 1911, i, 1065; from *Bull. Sci. Pharm.*, 1911, 18, 85—89).—The crystalline deposit from a percolate of cinchona bark with a mixture of glycerol, alcohol, and water consists exclusively of calcium quinate, and is free from alkaloids. Yvon's method for estimating the alkaloids by silicotungstic acid gives good results, the quinine salt having the formula



a light, yellow powder, which loses 6 mols. of water of crystallisation at 120°, and the composition of which remains constant under most diverse methods of precipitation.

S. B. S.

**Estimation of Nicotine in the Presence of Pyridine Bases.** LÉON SURRE (*Ann. Falsif.*, 1911, 4, 331—334).—The nicotine extract is, if necessary, diluted to about 10% strength of nicotine. Twenty-five to fifty c.c. of the solution (this depends whether the sample is alkaline or acid) are then distilled with addition of 1—2 grams of magnesium and 2—4 grams of powdered pumice in a special apparatus until 25 c.c. have passed over; water is now added continually to keep up the volume of the liquid, and the distillation is continued until exactly 150 c.c. of distillate has been collected; the receiver is then changed and another 150 c.c. is distilled off.

The first distillate contains all the pyridine with the bulk of the nicotine, which is then determined polarimetrically, pyridine being quite inactive. The second portion of the distillate contains the remainder of the nicotine, which is then titrated with standard acid, using luteol as indicator.

L. DE K.

**Estimation of Tannin in Wines.** PHILIPPE MALVEZIN (*Bull. Soc. Chim.*, 1911, [iv], 9, 620—621; *Ann. Chim. anal.*, 1911, 16, 221—222).—The method consists in precipitating the tannin as its zinc derivative, dissolving this in dilute sulphuric acid, and titrating with *N*/10-permanganate.

The zinc solution is made by dissolving 10 grams of zinc oxide in sufficient acetic acid, adding 80 c.c. of ammonia, and making up to 1 litre with distilled water. Ten c.c. of wine are mixed with 10 c.c. of the zinc solution; the mixture is boiled during five minutes, cooled, and 25 c.c. of boiling distilled water added. The precipitate is collected, washed with 100 c.c. of boiling distilled water, dissolved in dilute sulphuric acid (2.5 c.c. in 100 c.c. of distilled water), and titrated with *N*/10-permanganate at 60—70°, each c.c. of which is equal to 0.116 gram of gallotannic acid per litre of wine.

T. A. H.

**Lecithin.** ROBERT COHN (*Zeitsch. öffentl. Chem.*, 1911, 17, 203—217).—The fact that all the lecithin cannot be extracted with ether from commercial preparations of lecithin and yolk of egg may be attributed to an adsorption of this substance by the albumin. The whole of the adsorbed lecithin may be extracted with cold ethyl alcohol; it is not necessary to employ hot alcohol, as subsequent treatment with this liquid only removes traces of other phosphatides.

If the original preparation has been heated, it is not always possible to extract the whole of the lecithin with ether and alcohol or other liquids.

Lecithin may be estimated in preparations which contain added phosphoric or glycerophosphoric acids by extraction first with ether and then with alcohol. The alcoholic product contains some of the added acids, and must be re-extracted with chloroform to remove the soluble lecithin from these substances.

W. J. Y.

**Estimation of Aliphatic Amino-groups.** Applications to the Study of Proteolysis and Proteolytic Products. DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1911, 9, 185—204).—Full details of the apparatus and method previously described (*Abstr.*, 1910, ii, 751) are given. The nitric oxide is produced by the action of a feeble acid, for example, acetic acid, on sodium nitrite solution. The results are summarised as follows: Every known amino-acid obtained from proteins by acid hydrolysis reacts quantitatively with one and only one nitrogen atom, except lysine, which reacts with two, and proline and oxyproline, which do not react at all. All the amino-acids react with the whole of their nitrogen, except tryptophan, which reacts with half, histidine with one-third, arginine with one-fourth, and proline and oxyproline with none.

The dipeptides leucyl-leucine and leucylglycine, react with only their free amino-groups, the nitrogen in  $-\text{CO}\cdot\text{NH}-$  groups does not react. Glycyl anhydride does not give off nitrogen when treated with nitrous acid. The proteins egg-albumin and edestin evolve but little nitrogen. The proportion of free amino-nitrogen is twice as great in the primary albumoses, and still greater in the deutero-albumoses.

Purine and pyrimidine derivatives react normally with the exception of guanosine, which gives 1.25 instead of 1 mol. of nitrogen, probably owing to the rupture of the purine ring.

Glycine and nitrous acid yield, not only nitrogen, but also carbon dioxide, and this is not absorbed by the permanganate. The abnormal results obtained with glycine and glycylopeptides are most probably due to the fact that the intermediary diazo-compound does not decompose entirely in the normal manner, yielding glycolic acid, but that a part is completely decomposed, yielding carbon dioxide and other products, and the disintegration of the group at the end of the peptide chain severs the peptide linking and exposes to attack the nitrogen of the next amino-group.

Lysine reacts abnormally in requiring a longer time in order to react completely with the nitrous acid. This is probably due to the fact that one of the two amino-groups is not in the  $\alpha$ -position.

The method of amino-nitrogen determination has been used for measuring the rate of hydrolysis, using the ordinary equation for a unimolecular reaction. The method can also be used for determining the relative digestibility of proteins, for quantitative determination of proteolytic enzymes, for the analysis of amino-acids, for the determination of the complexity and structure of peptides and proteolytic products, and for the characterisation of proteins.

J. J. S.

**Estimation of Proline Obtained by the Ester Method in Protein Hydrolysis.** Proline Content of Casein. DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1911, 9, 205—207).—The usual method of estimating proline, namely, by the alcoholic extraction of the amino-acids, the esters of which boil below 90° under pressure of less than 1 mm. and calculating as proline all the soluble acids, gives too high results, as other soluble acids are also present. If, on the other hand, the proline is racemised and recrystallised as the *dl*-copper salt, only a portion of this can be separated from the mixture.

As proline does not give up its nitrogen when treated with nitrous acid, whereas the acids the esters of which distil over with proline do react with nitrous acid (compare preceding abstract), the following is a simple and accurate method for the determination of proline: the total nitrogen content of the mixture soluble in alcohol is determined, and this minus the amino-nitrogen as determined by nitrous acid gives the amount of nitrogen in the form of proline.

A specimen of casein examined by this method gave 6.7% of proline, a value about twice that given by Abderhalden. The amino-determination is the most delicate test for ascertaining the purity of proline isolated from mixtures of amino-acids.

J. J. S.

## General and Physical Chemistry.

**Index of Refraction of Binary Mixtures.** ARRIGO MAZZUCHELLI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 752—758).—In a detailed criticism of the work of Schweser (Abstr., 1910, ii, 913, 1039), the author points out that some of the regularities deduced by that writer are more apparent than real, inasmuch as they are in part necessary consequences of the mode of mathematical reduction employed.

R. V. S.

**Spectre-chemical Investigations. II. The Refraction and Dispersion of Substances Containing One Pair of Conjugate Double Linkings.** KARL AUWERS and FRITZ EISENLOHR (*J. pr. Chem.*, 1911, [ii], 84, 1—36).—The values of the specific refractions and dispersions of the compounds previously discussed (compare Abstr., 1910, ii, 365, 367, 561) have been re-calculated with the aid of Eisenlohr's recent values for the refractivities and dispersions of the various elements (this vol., ii, 81). With the aid of these and also of some additional data the following table is drawn up:

Compound.	Conjugate System.	Ex Ref.	Ex Disp., %
Aliphatic hydrocarbons .....	$\cdot\text{CH}:\text{CH}\cdot\text{CH}:\text{CH}\cdot$ .....	1.90	50
	$\cdot\text{CH}_2\text{CH}\cdot\text{CR}:\text{CH}\cdot$ .....	1.10	50
Styrenes .....	$\cdot\text{CH}=\text{C}:\text{CH}:\text{CH}\cdot$ .....	1.10	45
	$\cdot\text{CH}=\text{C}:\text{CR}:\text{CH}\cdot$ .....	0.70	30
	$\cdot\text{CH}=\text{C}:\text{CR}:\text{CR}\cdot$ .....	0.45	20
Hydroaromatic hydrocarbons..	$\text{CR}=\text{CH}-\text{CH}=\text{CR}\cdot$ .....	0.8 1.2	40 —
	$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CR}\cdot$ .....		
	$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{C}:\text{CH}\cdot$ .....		
	$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{C}:\text{CH}\cdot$ .....	0.25	20
Aldehydes .....	$\cdot\text{CH}:\text{CH}\cdot\text{CH}:\text{O}$ .....	1.80	50
	$\cdot\text{CH}:\text{CR}\cdot\text{CH}:\text{O}$ .....	1.25	45
	$\cdot\text{CH}:\text{CR}\cdot\text{CH}:\text{O}$ .....		
Cyclic aldehydes .....	$\cdot\text{CH}=\text{C}:\text{CH}:\text{O}$ .....	1.00	45
Ketones .....	$\cdot\text{CH}_2\text{CH}\cdot\text{CR}:\text{O}$ .....	0.90	30—40
	$\cdot\text{CR}:\text{CH}\cdot\text{CR}:\text{O}$ .....	0.85	
	$\cdot\text{CR}:\text{CR}\cdot\text{CR}:\text{O}$ .....	0.50	
Acids .....	$\cdot\text{CH}:\text{CH}\cdot\text{C}(\text{OH})_2\text{O}$ .....	1.10	40
	$\cdot\text{CH}:\text{CR}\cdot\text{C}(\text{OH})_2\text{O}$ .....	0.80	—
Esters .....	$\cdot\text{CH}:\text{CH}\cdot\text{C}(\text{OR})_2\text{O}$ .....	0.80	30
	$\cdot\text{CH}:\text{CR}\cdot\text{C}(\text{OR})_2\text{O}$ .....	0.50	20

As the value  $E\lambda_{\alpha}$  and  $E\lambda_{\beta}$  differ but little from one another, the mean value is given in the table, and similarly for  $E\lambda_{\gamma-\alpha}$  and  $E\lambda_{\beta-\alpha}$ , where  $E\lambda$  is the exaltation of  $\lambda$  (Abstr., 1910, ii, 365).

The following new experimental data are given:

$\alpha\beta$ -Diphenyl- $\Delta^2$ -hexene (Rupe and Bürgin, Abstr., 1910, i, 161) has b. p. 190—191°/11 mm.,  $D_4^{25}$  0.9892,  $n_D$  1.58083,  $n_D$  1.58749,  $n_F$  1.60490, and  $n_{\gamma}$  1.62049 at 22.8°.

1-Methyl-3-methenyl-1-cyclohexene,  $\text{CH}_2 \begin{matrix} \text{CMe}:\text{CH} \\ \text{CH}_2\text{---CH}_2 \end{matrix} \text{C}:\text{CH}_2$ , has b. p. 134—138°,  $D_4^{18}$  0.8389,  $n_D$  1.48274,  $n_D$  1.48723,  $n_F$  1.49872, and  $n_{\gamma}$  1.50910 at 17.0°.

The ethyl ether of methylisophoronocarboxylic acid (Merling and Welde, Abstr., 1909, i, 480) has b. p. 150—151°/14 mm.,  $D_4^{18}$  1.0248,  $n_D$  1.47760,  $n_D$  1.48181,  $n_F$  1.49023, and  $n_{\gamma}$  1.49776 at 19°, and the ethyl ether of ethylisophoronocarboxylate has b. p. 163—166°/19 mm.,  $D_4^{18}$  1.0109,  $n_D$  1.47936,  $n_D$  1.48288,  $n_F$  1.49148, and  $n_{\gamma}$  1.49921 at 19°.

Crotonaldehyde has b. p. 103—104°,  $D_4^{17}$  0.8537,  $D_4^{21}$  0.8486,  $n_D$  1.43064,  $n_D$  1.43478,  $n_F$  1.44550, and  $n_{\gamma}$  1.45491 at 23.1°.

Citral has b. p. 114.6—115.6°/15.5 mm.,  $D_4^{18.5}$  0.8897,  $n_D$  1.48506,  $n_D$  1.48945,  $n_F$  1.50073, and  $n_{\gamma}$  1.51081 at 17.05°.

*cyclo*Citral (Tiemann and Schmidt, Abstr., 1901, i, 158) has b. p. 112—114°/29 mm.,  $D_4^{22}$  0.9566,  $n_D$  1.49341,  $n_D$  1.49707,  $n_F$  1.50689, and  $n_{\gamma}$  1.51575 at 13.3°.  $\alpha$ -Ionone has b. p. 146.5—147.5°/28 mm.,  $D_4^{23}$  0.9298,  $n_D$  1.49452,  $n_D$  1.49842,  $n_F$  1.50834, and  $n_{\gamma}$  1.51735 at 22.3°.

1-Methyl- $\Delta^1$ -cyclohexen-1-one (Knoevenagel, Abstr., 1895, i, 51) has b. p. 94.5—95.5°/22 mm.,  $D_4^{18}$  0.9707,  $n_D$  1.49137,  $n_D$  1.49547,  $n_F$  1.50624, and  $n_{\gamma}$  1.51573 at 18.7°.

Carvenone has b. p. 117—117.5°/19 mm.,  $D_4^{18.4}$  0.9302,  $n_D$  1.48093,  $n_D$  1.48457,  $n_F$  1.49361, and  $n_{\gamma}$  1.50175 at 16.25°.

Ethyl isophoronocarboxylate has b. p. 142—143°/10 mm.,  $D_4^{15}$  1.0332,  $n_D$  1.47711,  $n_D$  1.48054,  $n_F$  1.48905, and  $n_{\gamma}$  1.49635 at 16.9°.

Acetophenone has b. p. 83.5°/12 mm.,  $D_4^{18.2}$  1.0301,  $n_D$  1.52945,  $n_D$  1.53503,  $n_F$  1.54925, and  $n_{\gamma}$  1.56201 at 17.15°.

Geranic acid has b. p. 158°/14 mm.,  $D_4^{18.4}$  0.9518,  $n_D$  1.48284,  $n_D$  1.48695,  $n_F$  1.49758, and  $n_{\gamma}$  1.50690 at 20.2°.

Pure methyl benzoate free from chlorine has b. p. 83°/11 mm.,  $D_4^{16}$  1.0905,  $n_D$  1.51309,  $n_D$  1.51810,  $n_F$  1.53060, and  $n_{\gamma}$  1.54157 at 16°. Methyl geranate has b. p. 117°/14 mm.,  $D_4^{20}$  0.9220,  $n_D$  1.46770,  $n_D$  1.47143,  $n_F$  1.48106, and  $n_{\gamma}$  1.48929 at 19.1°. Ethyl itaconate has b. p. 111°/13 mm.,  $D_4^{16.3}$  1.0500,  $n_D$  1.43833,  $n_D$  1.44114,  $n_F$  1.44765, and  $n_{\gamma}$  1.45334 at 15.4°.

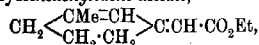
The high value for  $E\lambda_{\beta}$  obtained for  $\Delta$ - $\Delta^{2:8(9)}$ -*m*-menthadiene (Haworth, Perkin, and Wallach, Trans., 1911, 99, 123) is probably due to the compound examined containing a certain amount of an isomeride with a semicyclic double linking (compare Anwers and Peters, Abstr., 1910, i, 826, 841).

J. J. S.

Spectro-chemical Investigations. III. The Refraction and Dispersion of Hydrocarbons, Aldehydes, Ketones, Acids, and Esters containing Several Related Conjugations. KARL AUWERS and FRITZ EISENLOHR (*J. pr. Chem.*, 1911, [ii], 84, 37—121. Compare preceding abstract).—The theoretical values have been calculated

with the aid of Eisenlohr's recent numbers (this vol., ii, 81). Straight chains of conjugate linkings are termed "grouped conjugations," and systems of the types  $\begin{array}{c} \text{C:C} < \text{C:C} \\ \text{C:C} < \text{C:C} \end{array}$  and  $\begin{array}{c} \text{C:C} < \text{C:C} \\ \text{C:C} < \text{C:C} \end{array}$  are termed "crossed conjugations." Difficulties are involved in the investigation of many of these compounds, as they are unstable and readily form additive compounds. Many of the examples given are taken from chemical literature. The following data are new: *allo*Ocimene,  $\text{CHMe}_2\cdot\text{CH}:\text{CH}:\text{CH}:\text{CMe}:\text{CH}:\text{CH}_2$ , has  $D_4^{155}$  0.8119,  $n_D$  1.54403,  $n_D$  1.54558,  $n_D$  1.57682, and  $n_D$  1.60086. Its exaltation for  $\Sigma_{\gamma-\alpha}$  is 178%, and it cannot possibly be stereoisomeric with ocimene, as suggested by Enklaar. Pure  $\alpha$ -phenyl- $\delta$ -methyl- $\Delta^{\gamma\gamma}$ -pentadiene, after removal of all unaltered ketone, has b. p. 123—124°/14 mm.,  $D_4^{152}$  0.9512,  $n_D$  1.5409,  $n_D$  1.5474,  $n_D$  1.5651,  $n_D$  1.5923 at 16.2°. Di- $\alpha$ -phenyl- $\Delta^4$ -heptylene (Klages and Heilmann, Abstr., 1904, i, 487) has  $D_4^{\alpha}$  0.9673 and  $n_D$  1.5648 at 18°. Methylstyrylfulvene (Abstr., 1907, i, 639) has b. p. 87.4—87.9°/40 mm.,  $D_4^{209}$  0.8772,  $n_D$  1.52988,  $n_D$  1.53702 at 20.9°; diethylfulvene has b. p. 96.8—97.2°/40 mm.,  $D_4^{184}$  0.8812,  $n_D$  1.52339,  $n_D$  1.52997 at 16.4°; crotonylideneacetone (Meerwein, Abstr., 1908, i, 90) has b. p. 88°/28—29 mm.,  $D_4^{187}$  0.8946,  $n_D$  1.50924,  $n_D$  1.51767,  $n_D$  1.53858 at 18.9°; styryl phenyl ketone,  $D_4^{181}$  1.0712,  $n_D$  1.63422,  $n_D$  1.64578,  $n_D$  1.68161 at 62.3°; styryl methyl ketone, b. p. 126—128°/9 mm.,  $D_4^{173}$  1.0076,  $n_D$  1.57301,  $n_D$  1.58241,  $n_D$  1.60621 at 47.3°;  $\alpha$ -methylstyryl ethyl ketone, b. p. 124.5—125°/10 mm.,  $D_4^{173}$  1.0072,  $n_D$  1.56445,  $n_D$  1.57202,  $n_D$  1.59406 at 40.2°; benzylideneacetylacetone (Knoevenagel, Abstr., 1895, i, 50), b. p. 172—173.5°/12 mm.,  $D_4^{173}$  1.0928,  $n_D$  1.5762,  $n_D$  1.58464,  $n_D$  1.6083 at 17.3°;  $\beta$ -ionone, b. p. 150—151°/24 mm.,  $D_4^{196}$  0.9445,  $n_D$  1.51443,  $n_D$  1.51977,  $n_D$  1.53396,  $n_D$  1.54783 at 18.9°. The two modifications of benzophenone have much the same values (compare Eykman, *Rec. trav. chim.*, 1895, 14, 189).

Ethyl  $\alpha$ -methylcinnamate has b. p. 162—163°/30 mm.,  $D_4^{196}$  1.0321,  $n_D$  1.54074,  $n_D$  1.54753,  $n_D$  1.565,  $n_D$  1.58162 at 20.6°; ethyl  $\beta$ -methyl cinnamate, b. p. 138—138.5°/9 mm.,  $D_4^{196}$  1.0392,  $n_D$  1.5393,  $n_D$  1.54558,  $n_D$  1.56165,  $n_D$  1.57654 at 16.6°; ethyl  $\alpha$ -benzylcinnamate, m. p. 38—39°, b. p. 227—229°/30 mm.,  $D_4^{196}$  1.0831,  $n_D$  1.58163,  $n_D$  1.5885,  $n_D$  1.60717 at 16.1°; ethyl  $\alpha$ -phenylcinnamate, m. p. 28°, b. p. 214—215°/28 mm.,  $D_4^{152}$  1.0971,  $n_D$  1.58973,  $n_D$  1.59723,  $n_D$  1.61959 at 18.55°; ethyl benzylidenemalonate, b. p. 189—190°/14 mm.,  $D_4^{196}$  1.1045,  $n_D$  1.53242,  $n_D$  1.53894,  $n_D$  1.55697,  $n_D$  1.57444 at 20.4°. Ethyl 1-methyl- $\Delta^1$ -cyclohexenylidene acetate,



obtained by the action of zinc on a benzene solution of methylcyclohexenone and ethyl bromoacetate and heating the resulting hydroxy-ester with potassium hydrogen sulphate (compare Auwers and Peters, Abstr., 1910, i, 841), has, after purification by conversion into the acid and subsequent esterification, b. p. 133.5—135°/15 mm.,  $D_4^{189}$  0.9987,  $n_D$  1.52646,  $n_D$  1.53312,  $n_D$  1.55148, and  $n_D$  1.5694 at 17.3°.

Ethyl atropate,  $\text{CH}_3\cdot\text{CPh}\cdot\text{CO}_2\text{Et}$ , prepared from the silver salt, has b. p. 124—124.4°/16 mm., or 120.2—120.4°/14 mm.,  $D_4^{181}$  1.0508,  $n_D$  1.52151,

$n_D$  1.52605,  $n$  1.53871, and  $n$  1.54995 at 16.3°. *Iso*Propyl cinnamylidenacetate,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{C}_3\text{H}_7$ , is a yellow oil, with b. p. 169°/9 mm.,  $D_4^{20}$  1.0256,  $n_D$  1.59449,  $n_D$  1.60663,  $n_D$  1.64244 at 13.7°.

*Amyl cinnamylidenemalonate*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{C}_5\text{H}_{11})_2$ , has b. p. 212—214°/12 mm.,  $D_4^{20}$  1.087,  $n_D$  1.60221,  $n_D$  1.61599,  $n_D$  1.65914 at 19.8°. Ethyl cinnamylidenemalonate (Knoevenagel, Abstr., 1888, i, 406) has b. p. 217—220°/18 mm.,  $D_4^{20}$  1.0823,  $n_D$  1.60433,  $n_D$  1.6155,  $n_D$  1.66216 at 17.4°. Ethyl sorbate,  $\text{CHMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ , has b. p. 76°/14 mm.,  $D_4^{20}$  0.956,  $n_D$  1.49554,  $n_D$  1.50227,  $n_D$  1.52001,  $n_D$  1.53664 at 20.15°.

Ethyl  $\beta\delta$ -dimethylsorbate (compare Rupe and Lots, Abstr., 1903, i, 229) has b. p. 105.5—107°/30 mm.,  $D_4^{20}$  0.9281,  $n_D$  1.46165,  $n_D$  1.46548,  $n_D$  1.47513,  $n_D$  1.48385 at 16.7°. Ethyl fumarate has  $D_4^{20}$  1.0537,  $n_D$  1.43828,  $n_D$  1.44150,  $n_D$  1.44933,  $n_D$  1.45623 at 15.4° (compare Knops, Abstr., 1888, 938; 1889, 198). Methyl citraconate has b. p. 94—95°/11 mm.,  $D_4^{20}$  1.1248,  $n_D$  1.44788,  $n_D$  1.45107,  $n_D$  1.459,  $n_D$  1.46583 at 17.2°. Ethyl citraconate has b. p. 107.5—108°/11 mm.,  $D_4^{20}$  1.0444,  $n_D$  1.44326,  $n_D$  1.44630,  $n_D$  1.45351,  $n_D$  1.45967 at 41.9°. Koop's value for D is incorrect; the new value gives results for the exaltation of refraction and dispersion which agree with those for the methyl ester. Ethyl isopropylidenemalonate has b. p. 104—105.5°/15 mm. or 97—98.5°/13 mm.,  $D_4^{20}$  0.9959,  $n_D$  1.44915,  $n_D$  1.45223,  $n_D$  1.46024,  $n_D$  1.46729 at 19.9°. Ethyl ethylidenemalonate, prepared by condensing ethyl malonate and acetaldehyde with acetic anhydride and zinc chloride, has b. p. 117—118°/17.5 mm.,  $D_4^{20}$  1.0426,  $n_D$  1.43798,  $n_D$  1.44084,  $n_D$  1.44785,  $n_D$  1.45393 at 16.1°. Ethyl isopropylidenemalonate has b. p. 110.5—111.5°/9 mm.,  $D_4^{20}$  1.0284,  $n_D$  1.44562,  $n_D$  1.44857,  $n_D$  1.45602,  $n_D$  1.46233 at 17°.

Compounds with grouped conjugations show a much greater exaltation than those with crossed conjugations, and the introduction of substituents tends to reduce the exaltations.

The following table gives a list of the mean values for the exaltations of refraction and dispersion for some of the more important groups.

	Grouping.	$E\Delta$ Ref.	$E\Delta$ Disp., %
Hydrocarbons .....	$\cdot\text{CH}\cdot\text{CR}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot$	3.4	130
„ Phenylstyrene group..	$\begin{array}{c} \text{CH} \\ \diagup \quad \diagdown \\ \text{C}^{\text{C}}\text{C}^{\text{C}} \\ \diagdown \quad \diagup \\ \text{CH} \end{array}$	1.0	40
Aldehyde .....	$\cdot\text{CH}\cdot\text{CR}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{O}$	3.3	150
Ketones .....	$\cdot\text{CH}_2\cdot\text{CR}\cdot\text{CH}\cdot\text{CH}\cdot\text{CR}\cdot\text{O}$	3.3	145
„	$\cdot\text{CH}\cdot\text{CR}\cdot\text{CH}\cdot\text{CH}\cdot\text{CR}\cdot\text{O}$	2.7	110
„	$\cdot\text{CH}\cdot\text{CR}\cdot\text{CH}\cdot\text{CR}\cdot\text{CR}\cdot\text{O}$	2.1	95
„ (benzophenone group) .....	$\begin{array}{c} \text{CH} \\ \diagup \quad \diagdown \\ \text{C}^{\text{C}}\text{C}^{\text{C}} \\ \diagdown \quad \diagup \\ \text{CH} \end{array}$	1.0	45
„	$\cdot\text{CH}\cdot\text{CR}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}(\text{OR})\cdot\text{O}$	2.4	120
Esters .....	$\cdot\text{CH}\cdot\text{CR}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}(\text{OR})\cdot\text{O}$	2.0	100
„	$\cdot\text{CH}\cdot\text{CR}\cdot\text{CH}\cdot\text{CR}\cdot\text{C}(\text{OR})\cdot\text{O}$	1.5	75
„	$\begin{array}{c} \text{CH} \\ \diagup \quad \diagdown \\ \text{C}^{\text{C}}\text{C}^{\text{C}} \\ \diagdown \quad \diagup \\ \text{C}(\text{OR})\cdot\text{O} \end{array}$	0.5	25

The esters of cinnamylidene-acetic, -malonic, and -acetoacetic acids have especially high exaltations. That for the refractions  $\Sigma_D$  varies from 3.52 to 4.18, and for the dispersion  $\Sigma_\beta - \Sigma_\alpha$  from 210 to 313%.

Several examples are quoted from chemical literature which appear to be exceptions to some of the generalisations. In most cases the authors suggest that the abnormal values may be due to impurity or to the fact that the compound has not the structural formula usually accepted. Among the examples discussed are: hexatriene, tropilidene (Willstätter, Abstr., 1901, i, 223), and phenyl propenyl ketone (Kohler, Abstr., 1909, i, 940), which are presumably impure;  $\beta$ -ionone and eucarvone, both of which give much smaller exaltations than expected: this may be due to the presence of the  $\text{CMe}_2$  group; 1-methyl-1-dichloromethylcyclo- $\Delta^{2:3}$ -hexadien-2-one (Auwers and Hayden, Abstr., 1909, i, 592), which gives exceptionally low exaltations, probably due to the  $\text{CMe}\cdot\text{CHCl}_2$  group; phorone, which gives high exaltations, a result probably due to the presence of certain amounts of the unsymmetrical isomeride  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CMe}_2$ . J. J. S.

Applications of the Doctrine of Finite Increments of Energy to Physico-chemical Questions. JOHANNES STARK (*Zeitsch. Elektrochem.*, 1911, 17, 420—421).—The author calls attention to his earlier papers (Abstr., 1908, ii, 138; 1909, ii, 106, 109).

T. E.

[Spectroscopy of Oxygen.] HEINRICH KAYSER (*Ann. Physik*, 1911, [iv], 35, 608—612).—Polemical in reply to Steubing (this vol., ii, 558) and Stark (this vol., ii, 558).

H. M. D.

The Absorption of Light by Inorganic Salts. I. Aqueous Solutions of Cobalt Salts in the Infra-Red. ROBERT A. HOUSTOUN (*Proc. Roy. Soc. Edin.*, 1911, 31, 521—529).—The absorption of infra-red rays emitted by a Nernst filament has been measured for solutions of cobalt fluoride, chloride, bromide, iodide, nitrate, and sulphate. An increase of either the concentration or the temperature causes an increase of the extinction-coefficient at each end of the region examined, intermediate values being almost unchanged. The sulphate is an exception, absorbing slightly less in more concentrated solutions.

C. H. D.

The Absorption of Light by Inorganic Salts. II. Aqueous Solutions of Cobalt Salts in the Visible Spectrum. ROBERT A. HOUSTOUN and ALEXANDER R. BROWN (*Proc. Roy. Soc. Edin.*, 1911, 31, 530—537).—The absorption of solutions of cobalt salts in the visible spectrum is increased by rise of concentration or of temperature, as in the infra-red (compare preceding abstract).

C. H. D.

The Absorption of Light by Inorganic Salts. III. Aqueous Solutions of Nickel Salts in the Visible Spectrum and the Infra-Red. ROBERT A. HOUSTOUN (*Proc. Roy. Soc. Edin.*, 1911, 31, 538—546). The absorption of aqueous solutions of nickel fluoride, chloride, bromide, iodide, nitrate, and sulphate has been measured



throughout the visible and infra-red spectrum. In the case of the chloride and bromide, a great increase of absorption takes place in the violet when either the temperature or the concentration is increased.

C. H. D.

**The Absorption of Light by Inorganic Salts. IV. Aqueous Solutions of Nickel and Cobalt Salts in the Ultra-violet.** ROBERT A. HOUSTOUN and JOHN S. ANDERSON (*Proc. Roy. Soc. Edin.*, 1911, 31, 547—558).—A special form of quartz photometer is described for the photographic measurement of extinction-coefficients in the ultra-violet, using an iron arc as source of light.

The curves obtained by the thermopile, spectrophotometer, and photographic photometer join together well, completing the spectrum. The molecular extinction-coefficient is, to a first approximation, an additive quantity in the salts examined. The absorption bands in the infra-red must be due to the metal. The sulphates do not show bands due to the acid radicle, but bands appear in the ultra-violet region in the halides, and the nitrates and iodides show well-marked bands.

C. H. D.

**Absorption Spectrum of Aniline in the Ultra-violet.** HERMANN KOCH (*Zeitsch. wiss. Photochem.*, 1911, 9, 401—414).—The ultra-violet absorption spectrum of aniline vapour has been examined at temperatures between 15° and 80°. The spectrum, which exhibits a series of well-developed bands, extends further towards the red than the spectra of other benzene derivatives. The heads of the bands are on the violet side, and all of them are shaded off towards the red end. Changes of temperature, pressure, and thickness of the absorbing layer of vapour are without influence on the character of the band spectrum. Analysis of the wave-length measurements indicates that there are three distinct series of bands.

The absorption spectra obtained in the investigation of differently concentrated solutions of aniline in ethyl alcohol are also described.

H. M. D.

**Dynamic Isomerism.** HENRY E. ARMSTRONG, THOMAS M. LOWRY, SYDNEY YOUNG, CECIL H. DESCH, JAMES J. DOBBIE, MARTIN O. FORSTER, and ARTHUR LAPWORTH (*Brit. Assoc. Reports*, 1910, 80—81).—This report deals with the absorption spectra of camphor and its derivatives, in particular with the effect of the introduction of unsaturated groups ( $\cdot\text{CO}$ ,  $\cdot\text{CH}_2$ ,  $\cdot\text{CHPh}$ ,  $\cdot\text{CX}\cdot\text{OR}$ ) on the frequency and penetrating power of the absorption band.

T. S. P.

**Application of a Valency Hypothesis to Fluorescence.** JOHANNES STARK (*Zeitsch. Elektrochem.*, 1911, 17, 514—517).—A theoretical paper in which the author's hypothesis of the nature of valency (Abstr., 1908, ii, 574) is applied to explain fluorescence. An atom is regarded as a positively charged body, on the surface of which there are one or more negative electrons. When light is absorbed, its energy is converted into kinetic energy of these electrons, which fly off to a greater or smaller distance from the atom storing up potential

energy. On the return journey of the electron towards the atom, the potential energy is converted partly into light, not necessarily of the same wave-length as that absorbed. This is the explanation of fluorescence. The author's experiments have shown that fluorescence is always accompanied by ionisation of the substance. The effect of diluting the fluorescent substance with other substances is also discussed; the diminution of fluorescence which is always observed is in accordance with the theory, part of the energy of the electrons being absorbed by the diluting molecules.

T. E.

**Spectro-photometric Investigation of the Opalescence of a Simple Substance in the Neighbourhood of the Critical Condition.** W. H. Keesom (*Ann. Physik*, 1911, [iv], 35, 591—598).—The diffuse scattering of light rays by ethylene at temperatures slightly above the critical temperature has been investigated in reference to the cause of the opalescence effect. The variation of the intensity of the light, emitted at right angles to the incident beam, with the increase of the temperature above the critical temperature, and the magnitude of the coefficient of scattering are considered to support the explanation put forward by Smoluchowski (*Ann. Physik*, 1908, [iv], 25, 205). According to this, the opalescence is determined by density differences, the existence of which is rendered evident by a statistical consideration of the molecular movements.

H. M. D.

**New Type of Abnormal Rotation Dispersion. Contribution to Optical Superposition.** LEO TSCHUGAEFF (*Ber.*, 1911, 44, 2023—2030).—The type of abnormal rotation dispersion described by Biot embraces mixtures of two optically active substances which possess opposite rotatory powers and have different dispersions; it may be termed extramolecular.

1-Menthyl *d*- $\beta$ -camphorsulphonate is an example of a type the two constituents of which rotate in opposite directions, and have different although normal dispersions; in contrast to the type described by Biot, it may be termed intramolecular. The crystalline ester is faintly levorotatory, and has an abnormal rotatory dispersion, the curve showing a maximum between *E* and *F* both in acetone and toluene.

1-Menthyl 1- $\beta$ -camphorsulphonate, on the other hand, is strongly levorotatory, and has a perfectly normal dispersion.

The abnormality in the case of the *d*-camphorsulphonate is due to a partial compensation of the partial rotations in the molecule.

E. F. A.

**The Selective Photo-electric Effect for Metals Outside the Alkali Group.** ROBERT POHL and P. PRINGSHEIM (*Ber. Deut. physikal. Ges.*, 1911, 13, 474—481. Compare Abstr., 1910, ii, 379, 472, 922; this vol., ii, 90, 363).—The investigation of the photo-electric properties of barium shows that this exhibits a selective effect similar to that which has been already observed in the case of the alkali metals. For barium the selective maximum corresponds with the wave-length  $280\mu$ . In reference to the question of the cause of the selective

effect, the authors have examined the behaviour of mercury, lead, thallium, tin, cadmium, and bismuth, none of which exhibits selective action for wave-lengths greater than  $200\mu$ , which is the lowest wave-length attainable with the use of quartz apparatus. As regards the normal photo-electric effect of these metals, it is found that the range of sensibility extends further towards the visible spectrum the more easily oxidisable the metal.

H. M. D.

**Calculation of the Frequencies of the Electrons Giving Rise to the Selective Photo-electric Effect.** F. A. LINDEMANN (*Ber. Deut. physikal. Ges.*, 1911, 13, 482—488. Compare preceding abstract).—On the assumption that the electrons responsible for the selective effect are caused to rotate in elliptical paths round the positively charged ions by the active ultra-violet light, the author shows that the wave-length of the resonance maximum can be obtained from the formula  $\lambda = 65.3 \sqrt{a/n}$ , in which  $a$  is the atomic volume and  $n$  the valency of the metal. The calculated values for sodium, potassium, rubidium, and barium are in good agreement with the experimental determinations.

In accord with experiment, it is also shown that the wave-lengths of the resonance maxima are less than  $200\mu$ , except in the case of the alkali and alkaline earth metals. The wave-length range corresponding with the selective effect increases as the frequency of the resonance maximum increases, and when the active metal is alloyed with a second metal its resonance frequency increases more and more as the second metal becomes more electro-negative.

H. M. D.

**Ionic Mobility in Gases. I.** MAX REINGANUM (*Physikal. Zeitsch.*, 1911, 12, 575—580).—The author takes exception to Wellisch's explanation (this vol., ii, 358) of the large mobility exhibited by heavy ions, like methyl iodide and mercuric iodide, when moving in an electric field through a gas of low density. By means of a detailed analysis of Langevin's formula, it is shown that the heavy gas ions are in all probability represented by entities of molecular weight which corresponds with the chemical formula.

H. M. D.

**Electric Conductivity of Salt Vapours.** GERHARD C. SCHMIDT (*Ann. Physik.*, 1911, [iv], 35, 401—443).—The electric conductivity of the vapours of various salts and organic substances has been investigated. The apparatus consisted of a quartz or hard glass tube, which could be exhausted and heated electrically; the one electrode consisted of a large platinum cylinder, the other of a short platinum wire suspended along the axis of the cylinder. The substance to be examined was placed at the bottom of the tube and volatilised by raising the temperature of the heating jacket.

Preliminary qualitative experiments showed that the vapours of the halogen salts of zinc, cadmium, iron, aluminium, and ammonium are electrical conductors, whilst the vapours of iodine, mercury, arsenic, stannic chloride, mercuric chloride, bromide and iodide and of all the organic substances examined are non-conductors.

The conductivity of the halogen salt vapours varies considerably

with the time during which they are heated. In the case of cadmium salts the conductivity decreases from the commencement and tends towards a lower limiting value, but for the other halogen salts the decrease in conductivity is preceded by a rise to a maximum value.

Various experiments are described, the object of which was to ascertain the nature of the conducting ions and the mode of their formation. These experiments show that the ions are not the result of chemical decomposition of the solid substance, but are formed from the vapour itself. The presence of water vapour or oxygen has no influence on the formation of the ions, and the phenomenon cannot be attributed to the presence of traces of a radioactive substance.

The decrease of conductivity with time is found not to be due to fatigue effects, such as are exhibited by photo-electrically active metals. When a current is passed through the salt vapour, the conductivity diminishes more rapidly than in the absence of a current. As time goes on, the mobility of the ions decreases as a result of their combination with neutral molecules, and results are described which indicate that the positive ions are chiefly affected by this process. In addition to the combination of the ions with neutral molecules, the principal changes taking place in the salt vapour are considered to be represented by  $\text{CdI}_2 = \text{Cd}'' + 2\text{I}'$ ;  $\text{Cd}'' + 2\text{I}' = \text{Cd}'' + \text{I}_2''$ . The difference in the rates at which these changes occur is supposed to be responsible for the observed differences between cadmium salts and the halogen salts of the other metals.

The conductivity of the vapours increases rapidly with rise of temperature. At low potentials the current through the vapour is proportional to the applied voltage, but a saturation current is obtained when the voltage is increased sufficiently. At still higher potentials, ions are formed as the result of molecular collision, and this stage is succeeded by luminous discharge.

At low temperatures the nature of the equilibrium in the vapour and the resulting conductivity is influenced by the previous history of the substance under examination. Under these conditions an increase of the surface of the substance undergoing volatilisation leads to an increase in the observed conductivity. H. M. D.

**Electrode Potentials in the Electrolytic Manufacture of Chlorine and Alkali.** R. SACERDOTI (*Zeitsch. Elektrochem.*, 1911, 17, 473—478).—In technical processes using diaphragms, hot saturated solutions of sodium chloride are used in order to diminish the voltage required. The author has determined the effect of temperature on the potential difference between anodes of platinum and magnetite and cathodes of iron and platinum and the solutions during the passage of current.

The cathode potential is hardly affected by rise of temperature, but the anode potential is reduced by raising the temperature from 20° to 100° by from 0.4 to 0.8 volt. T. E.

**Nature of Electrolytic Dissociation and Solution Pressure.** FRIEDRICH KÄTZER (*Zeitsch. Elektrochem.*, 1911, 17, 453—466).—Gases are ionised either by collisions with rapidly moving electrons

or ions, or by Röntgen rays or ultra-violet light. The first cause cannot be operative in the case of liquids, consequently analogy leads to the view that they are ionised by some kind of radiation. At the ordinary temperature this must be of long wave-length. The density of radiation in a medium is proportional to the cube of its refractive index or to the 1.5 power of its dielectric constant. Each medium contains molecules the vibrations of which are in equilibrium with the radiation in the medium; they are resonators for the radiation. The larger the number of these the higher is the dielectric constant. The author attempts to show that an electrolyte may be ionised by having the vibrations of these resonators communicated to it, and also that a metal in contact with such a medium will give out ions in a similar way; the analogy to the ionisation of metals by ultra-violet light is pointed out. A quantitative application of these views leads to the conclusion that the dissociation constants of an electrolyte in two different solvents are in the ratio of the cubes of the dielectric constants of the solvents, which is in agreement with Walden's experimental results. It also follows that the solution tensions of metals and the solubility of salts should increase with the dielectric constants of the medium.

T. E.

**Maximum Tension of Electrolytic Valve Action in Fused Salts.** GÜNTHER SCHULZE (*Zeitsch. Elektrochem.*, 1911, 17, 509—514).

—The experiments with aqueous solutions (this vol., ii., 366) have now been extended to fused salts. The majority of the experiments were made with tantalum. The valve action occurs in fused salts in much the same way as in aqueous solutions. The maximum potential is, however, lower in a fused salt than the lowest maximum observed in aqueous solution with the same salt. The rate of development of the action diminishes as the temperature rises, until at high temperatures the action does not take place. For aqueous solutions the author has found that the maximum potential is independent of the temperature (the concentration of the ions being constant) and of the nature of the metal used as electrode. Assuming that the relation between ionic concentration and maximum potential found in aqueous solutions holds for the fused salts, it is possible to draw conclusions about their degree of dissociation from the maximum potentials observed. The results lie between 5% for ammonium nitrate fused at 167° and 56% for silver nitrate at 208°.

Aluminium shows approximately the same maximum-potentials as tantalum, but it is very sensitive to traces of moisture in the salts.

T. E.

**Behaviour of Carbon Dioxide and of Some Mixtures of Gases in the High Tension Electric Flame.** WILHELM MUTHMANN and A. SCHAIDHAUF (*Zeitsch. Elektrochem.*, 1911, 17, 497—503).—Muthmann and Hofer (Abstr., 1903, ii, 206) measured the temperature of the electric flame by means of the dissociation of carbon dioxide in its path. In the present paper experiments are described with electric flames produced in pure carbon dioxide between electrodes of gold, silver, and platinum. The flame is produced by means of a

transformer, the primary circuit of which is supplied with alternating current. When the current in the primary circuit is kept constant (12 amperes) and the length of the arc varied (from 2 mm. up to 2 cm.), the degree of dissociation of the carbon dioxide decreases from 22% to 0.7% with silver and gold electrodes. Platinum electrodes give the same results with arcs longer than 7 mm., but short arcs give very much smaller dissociations (0.4% at 2 mm., for example), obviously owing to the catalytic effect of the platinum on the re-combination of carbon monoxide and oxygen. The authors draw the conclusion that, owing to this re-combination, the degree of dissociation observed is always smaller than that corresponding with the temperature of the flame itself.

Experiments on the formation of nitric oxide from mixtures of nitrogen and carbon dioxide show that the nitrogen only reacts with the oxygen formed by dissociation of the carbon dioxide, and the production of nitric oxide is therefore small.

Mixtures of nitrogen and methane are also investigated. In order to avoid deposition of carbon, the mixtures are diluted with hydrogen so as to contain less than 10% of methane; from 2 to 3 molecules of nitrogen per mol. of methane are employed. In these circumstances the methane is converted quantitatively into hydrogen cyanide, independently of the nature of the electrodes or the size of the flame.

T. E.

**The Influence of Temperature on the Magnetic Properties of a Graded Series of Carbon Steels.** MARGARET B. MOIR (*Proc. Roy. Soc. Edin.*, 1911, 31, 505—516).—The magnetic quality of steel and cast iron improves with increase of temperature from 15° to 190°, diminishing from 200° onwards, and afterwards again improving. The transformation point at about 200° becomes less marked as the carbon is lessened, and is not observed in soft iron containing 0.06% C. It does not appear in the curves obtained by previous observers, the necessity of submitting the specimen to a series of reversals at the testing temperature (Ross and Gray, this vol., ii, 183) not having been recognised.

C. H. D.

**Magnetisation Coefficients of Gold.** MAURICE HANRIOT and FRANÇOIS RAOULT (*Compt. rend.*, 1911, 153, 182—185).—The properties of the brown ( $\beta$ ) modification of gold, which is obtained by the action of nitric acid on gold-silver alloys, have been investigated by measurements of its coefficient of magnetisation. By repeated treatment with nitric acid, traces of iron are removed, and the magnetisation coefficient increases. The highest values obtained for the brown gold and the yellow form prepared from the former by fusion were  $-0.181$  and  $-0.234 \times 10^{-6}$  respectively. Conversion of the brown into the yellow modification begins at about 350°, and is completed in about two hours at 400°. Determinations of the magnetisation coefficients of samples of brown gold prepared from alloys containing widely different proportions of silver indicate that the percentage of the  $\beta$ -modification in the product increases with the amount of silver present in the original alloy.

H. M. D.

**Gaseous Explosions.** SIR WILLIAM H. FRERES, DUGALD CLERK, BERTRAM HOPKINSON, WILLIAM A. BONE, BURSTALL, HUGH L. CALLENDAR, ERNEST G. COKER, W. E. DALEY, HAROLD B. DIXON, RICHARD T. GLAZE BROOK, J. E. PETAVEL, ARTHUR SMITHells, W. WATSON, JOHN A. HARKER, H. C. L. HOLDEN, H. R. SANKRY, DAVID L. CHAPMAN, and H. E. WIMPERIS (*Brit. Assoc. Reports*, 1910, 199—227).—This report deals with the radiation from gases, practical effects of radiation, amount of radiation from flame, nature and origin of radiation from flames, molecular theory of radiation from gases, and transparency. It contains appendices on the radiation from flames [H. L. Callendar], on radiation in a gaseous explosion [B. Hopkinson], and abstracts from various papers relating to the application of heat radiation from luminous flames to Siemens' regenerating furnaces. T. S. P.

**Internal Pressure in Gases; Equations of State and the Law of Molecular Attraction.** ANATOLE LEBUQ (*Compt. rend.*, 1911, 153, 179—182. Compare Abstr., 1909, ii, 298, 381, 382, 550, 644).—The internal pressure of a gas diminishes with rise of temperature, but the variation cannot be represented either by the formula of Clausius or that of Sarrau.

From the internal pressure data, communicated previously, it is found that for gases of the same molecular complexity, when compared at low pressures and corresponding temperatures, the attraction between two molecules is proportional to the square of their mass, and inversely proportional to the fourth power of their distance apart. For diatomic gases, the attractive force is only about half as large as that for triatomic gases. H. M. D.

**Specific Heat of Gases.** KARL DRUCKER (*Zeitsch. Elektrochem.*, 1911, 17, 466—472).—The total energy,  $U$ , of a monatomic, or chemically unalterable, gas and its volume energy,  $F=RT$ , are related, thus:  $F=2/3U$ . This relation is usually obtained by means of the kinetic theory, but the author shows that it may be proved without the help of any assumption about the structure of the gas. The volume energy is, therefore,  $RT$  per mol., and the total energy is  $3/2RT$  for perfect monatomic gases. A polyatomic gas (containing  $\nu$  atoms per molecule) is imagined to be produced by condensation of  $\nu$  volumes of monatomic gas. For example, 3 mols. of monatomic gas possess  $3RT$  volume and  $9/2RT$  total energy; after condensation  $2RT$  of volume energy has disappeared, and the total energy is  $5/2RT$  at least, but it may be more if some part of the loss of volume energy has appeared as bound energy in the gas. Calling the ratio, increase of bound energy/loss of volume energy  $=\epsilon$ , the total energy of a polyatomic gas is  $U=RT[1+0.5\nu+(\nu-1)\epsilon]$ . The values of  $\epsilon$  calculated from the molecular heats of some 30 gases are about 0.5, and diminish slowly with the temperature, the temperature-coefficients being the same in groups of similar substances. Exceptions are explained by dissociation of the gases or molecular association. Putting  $\epsilon=0.5$ , the molecular heats at constant pressure and volume are,  $C_p=R(\nu+1.5)$ ,  $C_v=R(\nu+0.5)$ , and  $C_p/C_v=(\nu+1.5)/(\nu+0.5)$ . The

values calculated from these formulae agree very well with the observed values in a large number of cases. T. E.

**Critical Solution Temperatures of Liquids.** E. MOLES (*Anal. Nu. Quim.*, 1911, 9, 157—172).—Determinations of the critical solution temperatures of the systems water-isobutyric acid and water-phenol have been made by means of Smith and Menzies' dynamic isotenoscope (*Abstr.*, 1910, ii, 1038). The values are in close accord with those obtained by other workers. G. D. L.

**The Connexion between the Volatility, Fusibility, and Density of Compounds, and the Chemical Forces at Play within their Molecules.** GROFFREY MARTIN (*Chem. News*, 1911, 104, 29).—It is observed that the relationship between the density of compounds and the degree of chemical attraction between their atoms, pointed out by Richards (*Faraday Lecture*, Trans., 1911, 99, 1201), is only a particular case of a greater generalisation already noted by the author, namely, that "it is the internal chemical forces which the atoms exert on each other in the molecule which decides the external attractions with which the molecules themselves are attracted together, and consequently properties arising out of this molecular attraction, such as volatility, fusibility, hardness, and density of the compound." The assumption that the atoms are themselves compressed by the forces of chemical attraction is therefore regarded as questionable. J. D. K.

**The Viscosity of Certain Organic Liquids in the Condition of Turbulent Flow.** WALTER SORKAU (*Physikal. Zeitsch.*, 1911, 12, 532—595. Compare Bose and Rauert, *Abstr.*, 1909, ii, 645; E. and M. Bose, this vol., ii, 257).—Measurements have been made of the rate of flow of water, ethyl alcohol, chloroform, acetone, and amylene through a capillary tube under pressures sufficiently high to give rise to the turbulent condition. Whereas the product of pressure ( $p$ ) and time of outflow ( $t$ ) is constant for the state of steady flow, it increases in all cases with the pressure in the turbulent condition. Curves are plotted which show the variation of  $pt$  with  $p$  for the various liquids at different temperatures. In the case of chloroform, acetone, and amylene, the  $pt$  curves show distinct breaks at a particular pressure; this pressure diminishes as the temperature rises. A possible explanation of the transition phenomenon on molecular kinetic grounds is suggested. H. M. D.

**Isopiestic Expansibility of Water at High Pressures and Temperatures.** W. WATSON (*Proc. Roy. Soc. Edin.*, 1911, 31, 456—477).—Pure water attacks quartz glass strongly at high temperatures, and the experiments have therefore been made with water slightly acidified with hydrochloric acid, which does not affect the expansibility. An electrically heated vessel is used, enclosed in a cooled steel cylinder. The dilatometer is of quartz glass.

The rate of change of volume with temperature increases with temperature to a maximum, the value of which decreases with increase



of pressure. While liquid, water expands as an ordinary liquid. Above the critical temperature, the coefficient of expansion of water, like that of other gases, is independent of the temperature, and decreases with increase of pressure.

C. H. D.

Extension of the Laws of Capillarity to Cases where the Elements of the Capillary System are Mobile with Respect to One Another; Extension Leading to a New View of the Phenomena of Swelling of Dried Wood, of the Dissolution of Gums, Albumins, Etc., and of True Solutions. J. H. RUSSENERGER (*Compt. rend.*, 1911, 153, 57—60. Compare Abstr., 1910, ii, 189).—A theoretical discussion. The phenomena mentioned in the title are compared with the increase in height observed when a pile of thin laminae of mica, lead, etc., is moistened with water.

W. O. W.

Solubility. I. J. VARGAS EYRE (*Brit. Assoc. Reports*, 1910, 425—468).—The report classifies, both chronologically and according to subject, the literature on the subject of solubility, and contains a brief statement of the main conclusions arrived at by the various authors. It is divided into the following sections: I. Methods of determination: A, solids; B, liquids; C, gases. II. Influence of nature of solvent: A, physical; B, chemical. III. Influence of nature of solute: A, physical; B, chemical. IV. Solubility in relation to: (1) temperature, (2) heat of dissolution, (3) pressure, (4) influence of other substances: (i) non-electrolytes and non-electrolytes, (ii) non-electrolytes and electrolytes, (iii) electrolytes and electrolytes. V. Mutual solubility and distribution coefficients. VI. Theoretical considerations. VII. Chronological bibliography.

T. S. P.

Technical Soaps as Colloidal Solutions. J. LEIMDÖRFER (*Koll. Chem. Beihefte*, 1911, 2, 343—398).—The nature of the various processes incidental to the production of technical soaps is examined from the colloido-chemical point of view. The course of the saponification process, partial and total flocculation, swelling and dehydration, changes in viscosity, and the influence of different electrolytes on the production of soaps from various fats are discussed in detail. Other matters dealt with relate to the part played by the dispersive medium (water, glycerol, and alcohol) and to the adsorption of non-electrolytes and other colloidal substances.

H. M. D.

The Equilibrium  $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightleftharpoons \text{CaCO}_3 + \text{Na}_2\text{SO}_4$ . WALTER HERZ (*Zeitsch. anorg. Chem.*, 1911, 71, 206—208).—The constant  $[\text{Na}_2\text{CO}_3]/[\text{Na}_2\text{SO}_4]$  is found to be 0.054, the same value being reached from both sides. Concentrated solutions of sodium carbonate yield irregular values, owing to the formation of gaylussite,  

$$\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 5\text{H}_2\text{O}.$$

C. H. D.

Cæsium Nitrate and the Law of Mass Action. EDWARD W. WASHBURN and DUNCAN A. MACINNES (*Zeitsch. Elektrochem.*, 1911, 17, 503—509).—Bjltz (Abstr., 1902, ii, 310) has stated that cæsium

nitrate follows Ostwald's dilution law. This conclusion was drawn from measurements of the freezing points of aqueous solutions of the salt. The authors have redetermined the freezing points of solutions of cesium nitrate up to 0.45 normal. Calling  $n$  the number of gram-molecules dissolved in 1000 grams of water, the depressions of freezing point are given by  $\Delta t = 3.426n - 1.862n^2 + 1.373n^3$ . The dissociation, calculated from these results, follows Ostwald's law for strong solutions (0.2 to 0.5 normal), but does not follow it even approximately for dilute solutions.

T. E.

**Velocity of Hydrolysis of Glycerolphosphoric Acid.** FERNAND MALENGREAU and GEORGES PRIGENT (*Zeitsch. physiol. Chem.*, 1911, 73, 68—84).—The rate of hydrolysis of glycerolphosphoric acid by water at 100° has been determined by gravimetric estimation of the liberated phosphoric acid. The reaction, in the case of the free acid as well as in that of the acid potassium and sodium salts, is unimolecular, but the salts in question are decomposed about twice as fast as the free acid. On the other hand, when the acid is neutralised by a base, the salt is scarcely attacked by water. The explanation of these results is that  $H^+$  ions in small concentration (in this case resulting from the ionisation of the acid itself) accelerate the action, but in greater concentration they exercise a retarding effect. Acetic, hydrochloric, and sulphuric acids all retard the action. Salts of strong acids have mostly a slight accelerating effect, but salts of weak acids accelerate the reaction considerably. This is ascribed to a diminution in the  $H^+$  ion concentration, owing to double decomposition.

The rate of hydrolysis is greatly increased by rise of temperature.

G. S.

**Catalytic Oxidation of Phenols in Presence of Iron Salts.** H. COLIN and A. SÉNÉCHAL (*Compt. rend.*, 1911, 153, 76—79).—The addition of sulphuric acid to an artificial peroxydase system produces a diminution in the rate of oxidation of quinol in proportion to the amount added until a minimum is reached, after which the rate increases. The acceleration is probably due to the formation of a persulphuric acid. Weak organic acids show no minimum point. The retarding effect of acetic acid is only noticeable at high concentrations, whilst that of oxalic acid is much more pronounced in dilute solutions. Citric acid has an effect intermediate between these two. The retarding effect of acids is attributed to the formation of complex iron salts.

W. O. W.

**The Specific Action of Different Compounds of Iron from the Point of View of their Action as Peroxydases.** JULES WOLFF and ELOI DE STOECKLIN (*Compt. rend.*, 1911, 153, 139—141).—The authors maintain their thesis that the specific action of iron compounds in various reactions depends on the particular compound of iron (compare *Abstr.*, 1908, i, 490, 746; ii, 573, 1022; 1909, i, 347, 451) as against the views expressed by Colin and Sénéchal (preceding abstract), and give further experimental evidence in support thereof.

In the presence of an extremely small quantity of colloidal iron

ferrocyanide, hydrogen peroxide readily oxidises [it] to quinhydrone, whereas it is necessary to add a large excess of potassium thiocyanate to ferric thiocyanate to produce the same effect. Pyrogallol is similarly readily oxidised to purpurogallin in the presence of the ferrocyanide, whereas the mixture of the thiocyanates produces no effect.

Further experiments on the liberation of iodine from potassium iodide by hydrogen peroxide in acetic acid solution in the presence of various iron salts and potassium thiocyanate gave the following results: (1) If a salt of iron, such as the nitrate, sulphate, chloride, or acetate, acts as a catalyst in the above reaction, its catalytic power is considerably increased by the addition of small quantities of potassium thiocyanate. (2) The catalytic power increases rapidly with increasing quantities of thiocyanate, attaining a maximum when the composition  $K_2Fe(CNS)_6$  is reached. Further increase in the quantity of potassium thiocyanate has then very little effect.

It is possible that the accelerating effect of the thiocyanate may be due to the formation of persulphate by the oxidising action of the hydrogen peroxide, but the authors find that the addition of sodium persulphate in quantity exceeding that which would be formed during the reaction has no accelerating effect on the action of iron nitrate.

T. S. P.

**A Simple Valve for Water Pumps.** ROBERT BEHREND (*Chem. Zeit.*, 1911, 35, 807).—The valve is shown in the diagram. The tube *b* is fitted into *a* by means of india-rubber tubing, which projects past the end of *b* and so forms a seat for the stopper to press against when the valve acts.

T. S. P.



**An Improved Funnel.** PHILIP BLACKMAN (*Chem. News*, 1911, 104, 30).—A glass funnel of such a form that the lower portion of the paper cone does not touch the funnel itself, with the result that filtration is greatly accelerated.

J. D. K.

**A Funnel Support.** PHILIP BLACKMAN (*Chem. News*, 1911, 104, 30—31).—A concentrically fluted glass disk, having at the centre an upright tube for holding the funnel steadily. It may be used with beakers, etc., of various sizes, and protects the filtrate from dust.

J. D. K.

## Inorganic Chemistry.

**Active State of Chlorine Produced by Light.** GOTTFRIED KÜMMEL (*Zeitsch. Elektrochem.*, 1911, 17, 409—412).—An insulated platinum cylinder is placed inside a glass vessel, the walls of which are lined with platinum foil. The cylinder is charged positively to 200

volts, and it is in electrical connexion with an electroscope. The platinum foil is earthed. Any loss of the charge of the cylinder by leakage through the gas surrounding it is thus easily observed.

Moist or dry nitrogen, hydrogen, carbon dioxide, or oxygen, all give the same small rate of leakage whether they are in the dark or exposed to the light of an electric arc lamp. Pure, dry chlorine gives the same result, but moist chlorine gives a considerably larger leak in the dark, and this is still further increased by exposure to light. The effect increases with the quantity of water-vapour present. The addition of oxygen to the chlorine diminishes it. Air to which hydrogen chloride has been added in small quantity behaves in the same way as moist chlorine. The conductivity is therefore due to hydrogen chloride formed by the action of chlorine on water vapour.

The positive platinum cylinder was acted on in all cases in which the chlorine was a conductor, but not the earthed (or negative) platinum foil.

T. E.

**Influence of Current Concentration on the Formation of Chlorates by Electrolysis.** ERICH MÜLLER and PAUL KOPPE (*Zeitsch. Elektrochem.*, 1911, 17, 421—430).—According to Foerster and Müller's theory of the formation of chlorates, two reactions take place, the one being purely chemical, the other electrolytic. The latter converts hypochlorite ions into chlorate and oxygen gas at the anode, and therefore involves a loss of efficiency. The purely chemical action (the oxidation of hypochlorite ions by free hypochlorous acid), on the other hand, involves no loss of oxidising power. Anything that accelerates the purely chemical action without affecting the rate of the electrolytic one will, therefore, increase the efficiency of the process as a whole. Since the chemical action goes on throughout the mass of the solution, whilst the electrolytic action only takes place at the anode, it is fairly obvious that an increase of the volume of solution relatively to the current used will have this effect, and the authors show both on theoretical grounds and by a large number of experiments that this is the case.

T. E.

**Effect of the Frequency and Form of the Current on the Formation of Ozone.** GEDEON LECHNER (*Zeitsch. Elektrochem.*, 1911, 17, 414—420).—Very pure and dry oxygen was exposed to the silent discharge in a Berthelot ozoniser. The discharge was produced by a Ruhmkorff coil, through the primary circuit of which an interrupted direct current was passed. At first the times during which the current flowed and was interrupted were equal, the number of interruptions per second being varied from 12 to 48. In these circumstances the quantity of ozone produced per hour increased with the number of interruptions, but not in direct proportion to this number. There are two reasons for this: (1) Owing to the self-induction of the circuit the current does not reach its maximum value at once, and therefore the average current is smaller for the shorter periods than for the longer ones. (2) The concentration of ozone in the gas is greater with the larger number of interruptions, and therefore the quantity destroyed by the discharge is greater.

In a final set of experiments, the flow of oxygen through the ozoniser was varied, so that the concentration of ozone was always the same and the interrupter was arranged to give different numbers of current shocks each of the same duration per second.

With this arrangement the quantity of ozone produced per hour was very accurately proportional to the number of interruptions per second.

A comparison of the effects of supplying the primary of the coil with interrupted direct current and with alternating current, the *E.M.F.* curve of which was almost a sine curve, showed that the latter gave about 1/20th the quantity of ozone. This is due to the lower *E.M.F.* of the secondary current produced by the alternating current, a certain minimum *E.M.F.* being required to produce a discharge through the gas at all.

When, however, the apparatus was arranged so as to obtain equal effective currents in the secondary circuit, the alternating current gave larger yields of ozone than the direct current.

T. E.

**Action of Sulphuryl Chloride on Certain Metals.** H. B. NORTH (*Bull. Soc. chim.*, 1911, [iv], 9, 646—649).—Gold and platinum are attacked by sulphuryl chloride after prolonged heating with it in a sealed tube at 150°, anhydrous auric chloride and platonic chloride being formed together with sulphur dioxide. Silver, zinc, and cadmium do not react with sulphuryl chloride even at 300° (compare *Abstr.*, 1910, ii, 296). Iron behaves like platinum and gold, anhydrous ferric chloride being obtained in large crystals.

R. V. S.

**Iron as a Catalyst in the Synthesis of Ammonia under Pressure.** KARL JELLINEK (*Zeitsch. anorg. Chem.*, 1911, 71, 121—137).—An electric furnace, with nickel resistance wire, is described, which may be heated to 800—1000° under a pressure of 100 atmospheres for several hours. Nitrogen and hydrogen are admitted in theoretical proportions, iron being introduced as a contact material. The ammonia in the issuing gases is estimated by titration. Ammonia is not obtained when a porcelain vessel, not containing iron, is used. At 870°, iron dissolves or adsorbs considerable quantities of ammonia, so that the quantity of ammonia in the issuing gas increases rapidly as the pressure is diminished. Under these conditions the equilibrium concentration of ammonia in the mixture may be exceeded 100 times.

C. H. D.

**Can Thomsen's Thermochemical Method be Employed to Investigate the Hydration of Metaphosphoric Acid?** D. BALABEFF (*Zeitsch. anorg. Chem.*, 1911, 71, 70—72).—Experiments with an ice calorimeter show that when a solution of orthophosphoric acid is added to one of metaphosphoric acid, heat is at first absorbed and afterwards developed. Thomsen's method is therefore not applicable to the hydration of metaphosphoric acid.

C. H. D.

**The Hydrates of Arsenic Pentoxide.** D. BALABEFF (*Zeitsch. anorg. Chem.*, 1911, 71, 73—78).—When a solution of arsenic acid is evaporated in an open vessel at 50°, or under increased pressure at 150°, the crystals which separate always have the composition

$\text{H}_2\text{As}_2\text{O}_{10}$  or  $3\text{As}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ . Above  $200^\circ$ , crystals of the oxide,  $\text{As}_2\text{O}_5$ , separate directly. Concentrated solutions, crystallising spontaneously or by freezing, deposit crystals of the hydrate  $\text{H}_2\text{AsO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ , or mixtures of this with  $\text{H}_2\text{As}_2\text{O}_{10}$ . The hydrate,  $\text{H}_2\text{AsO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ , loses water on fusion, passing into  $\text{H}_2\text{As}_2\text{O}_{10}$ . The formation of any other hydrate was not observed.  
C. H. D.

**Gaseous Combustion.** WILLIAM A. BONE (*Brit. Assoc. Reports*, 1910, 469—505).—The report summarises the results of the principal researches upon the chemical aspects of gaseous combustion during the past thirty years, and is divided into the following sections: I, Ignition temperatures and the initial phases of gaseous explosions; II, the explosion wave; III, the pressures produced in gaseous explosions; IV, the influence of moisture on combustion; V, the combustion of hydrocarbons; VI, the influence of hot surfaces on combustion.  
T. S. P.

**The Formation of Potassium Nitrate by Double Decomposition from the Point of View of the Phase Rule.** ERNEST JANCKE (*Zeitsch. anorg. Chem.*, 1911, 71, 1—18).—The author's graphical method of representing the behaviour of reciprocal salt-pairs (Abstr., 1908, ii, 808) has been applied to the systems  $\text{NaCl-KNO}_3$ ,  $\text{KCl-NaNO}_3$  (Uyeda, Abstr., 1910, ii, 836), and  $\text{NaNO}_3\text{-K}_2\text{CO}_3$ ,  $\text{KNO}_3\text{-Na}_2\text{CO}_3$  (Kreman and Zitek, Abstr., 1909, ii, 572); the numerical data of these authors are utilised in constructing the diagrams. A method of converting percentages by weight in ternary systems into molecular percentages is also described, and several numerical examples are worked out.  
C. H. D.

**Properties of Potassium Nitrite.** EDUARD DONATH (*Chem. Zeit.*, 1911, 35, 773—774).—When 96% alcohol is added to an almost saturated solution of potassium nitrite, two liquid layers are formed, the lower aqueous layer containing 71.90%  $\text{KNO}_2$ , and the upper alcoholic layer, 6.9%  $\text{KNO}_2$ . When methyl alcohol is used, pure potassium nitrite is precipitated as a fine powder, and since potassium hydroxide is soluble in methyl alcohol, a convenient method is given for the separation of potassium hydroxide and potassium nitrite.

Methyl alcohol precipitates sodium hydroxide from concentrated solutions. Sodium nitrite is neither precipitated from its aqueous solutions by methyl alcohol, nor are two layers formed on the addition of ethyl alcohol.  
T. S. P.

**The Preparation of Pure Hyposulphites and the System Hyposulphite-Water.** KARL JELLINEK (*Zeitsch. anorg. Chem.*, 1911, 71, 96).—The salting-out of sodium hyposulphite takes place without difficulty, even when only small quantities of salt are used, if alkali is present, and this method is adopted in the technical preparation of the salt (compare this vol., ii, 278).  
C. H. D.

**Ammonium Carnallite.** WILHELM BILTZ and E. MARCUS (*Zeitsch. anorg. Chem.*, 1911, 71, 166—181).—In an investigation of the potash deposits (Abstr., 1909, ii, 571) it was observed that the

content of ammonia followed that of carnallite. It is now found that ammonium and potassium carnallites form solid solutions with one another.

The solubility of magnesium chloride in water at 25° is 104.5 mole. in 1000 mole., the value 108 adopted in the usual diagram being too high. The equilibrium of ammonium and magnesium chlorides in water has also been studied. In the preparation of the solutions in contact with two solid phases, a saturated solution of the one salt, containing crystals of that salt, is taken, and ammonium carnallite is added until the composition of the solution is not further changed. The point  $\text{NH}_4\text{Cl} | (\text{NH}_4)\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  is also observed by the appearance of anisotropic crystals together with the isotropic crystals. Ammonium carnallite, like the potassium compound, breaks up on the addition of a small quantity of water.

Potassium and ammonium chlorides form together two series of solid solutions, interrupted by a gap which extends from 20 to 98 mol. %  $\text{NH}_4\text{Cl}$  at 25°. This is confirmed by crystallographic examination.

Potassium and ammonium carnallites form three series of solid solutions, the first of the type of ordinary carnallite, extending to 15 mol. % of the ammonium salt, the second, of the type of ammonium carnallite, containing from 27 to 100 mol. % of that salt, and the third, containing from 15 to 27 mol. %, and crystallising in prisms, probably monoclinic, extinguishing at an angle of 27° to the direction of their length. C. H. D.

**Thermal Analysis of Binary Mixtures of the Chlorides of Univalent Metals.** CARLO SANDONNINI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 758—764).—The paper deals with the thermal analysis of the systems  $\text{NaCl}-\text{AgCl}$ ,  $\text{LiCl}-\text{AgCl}$ , and  $\text{LiCl}-\text{CuCl}$ . Sodium chloride and silver chloride give mixed crystals of one species only in all proportions (compare Botta, this vol., ii, 293).

Lithium chloride and silver chloride yield mixed crystals of two kinds, and the gap of miscibility extends from 16 mols. % to 50 mols. % of silver chloride, the temperature of the pause being 469°.

Lithium chloride and cuprous chloride also give mixed crystals of two species, and the gap of miscibility extends from 25 mols. % to 55 mols. % of cuprous chloride (temperature 424°). The curve of fusion of the mixed crystals rich in cuprous chloride presents a minimum at about 80 mols. % of cuprous chloride. R. V. S.

**The Compounds of Silver and Cadmium.** G. J. PETRENKO and A. S. FEDOROFF (*Zeitsch. anorg. Chem.*, 1911, 71, 215—218).—The authors' results (this vol., ii, 281) indicate the existence of four compounds of silver and cadmium,  $\text{AgCd}$ ,  $\text{AgCd}_2$ ,  $\text{Ag}_2\text{Cd}$ , and  $\text{AgCd}_3$ , whilst Bruni and Quercigh (Abstr., 1910, ii, 953) find the compound  $\text{AgCd}$ . Quenching experiments with the alloy containing 19.5% Ag show that at 480° the solid solution is in equilibrium with the liquid. A polygonal structure is not obtained on annealing. The compound  $\text{AgCd}_3$  is therefore to be rejected, and whilst the existence of the compound  $\text{AgCd}_2$  is probable, it is not fully established. C. H. D.

**The Periodides and Perbromides of the Alkaline Earth Metals.** WALTER HERZ and ALFRED BULLA (*Zeitsch. anorg. Chem.*, 1911, 71, 254—256).—Varying quantities of iodine are added to a solution of barium iodide in water, and the solution is then shaken with carbon tetrachloride at  $-25^{\circ}$ . The partition coefficient of the iodine is then determined. A constant is obtained for the value  $k = [\text{BaI}_2][\text{I}_2]/[\text{BaI}_4]$  over a considerable range of concentration, indicating the presence of the periodide. At high concentrations of iodine, high values are obtained for  $k$ , indicating the formation of higher polyiodides. In a similar manner, the formation of calcium and strontium periodides, and of barium and calcium perbromides, is demonstrated. C. H. D.

**Potassium Barium Orthothioarsenate,**  $\text{KBaAsS}_6 \cdot 6\text{H}_2\text{O}$ ;  $(\text{K}_2\text{AsS}_4 \cdot \text{Ba}_2\text{As}_2\text{S}_8 \cdot 18\text{H}_2\text{O})$ . EMANUEL GLATZEL (*Zeitsch. anorg. Chem.*, 1911, 71, 209—214).—Barium orthothioarsenate (this vol., ii, 282) reacts in a finely-powdered state with a solution of potassium chloride, yielding colourless crystals of *potassium barium orthothioarsenate*,  $\text{KBaAsS}_6 \cdot 6\text{H}_2\text{O}$ . The salt is more easily prepared by adding potassium chloride to the solution obtained by saturating barium hydrogen sulphide with arsenic pentasulphide. C. H. D.

**Zinc Peroxite (Zinc Moloxide, Zinc Peroxydate),**  $\text{ZnO}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$  and a General Method of Preparing Peroxites. ERICH EBELER and R. L. KRAUSE (*Zeitsch. anorg. Chem.*, 1911, 71, 150—165).—It is proposed to use the terms "peroxydate" for additive compounds of hydrogen peroxide, and "peroxite" for the true salts of hydrogen peroxide. The methods of preparing peroxites generally yield products containing added water or hydrogen peroxide. The pure compounds may be obtained by the action of a dry ethereal solution of hydrogen peroxide on the alkyl compounds of metals or on metal-amines.

A solution of hydrogen peroxide is extracted with ether, and the extract is dried with anhydrous sodium sulphate and added gradually to a cooled solution of zinc ethyl in dry ether. Ethane is evolved, and a white, amorphous precipitate is formed, which is washed with ether and dried in a vacuum.

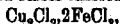
*Zinc peroxite*,  $\text{ZnO}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ , is slowly decomposed by acids, yielding hydrogen peroxide, or violently by heat, evolving oxygen. Water hydrolyses it very slowly, an equilibrium being reached. The compound acts on a photographic plate.

For the estimation of zinc, the peroxite is dissolved in dilute sulphuric acid. Oxygen is estimated by titration with permanganate, the oxygen evolved being also measured. Water is estimated by heating in dry air. C. H. D.

**The Combining Power of the Chlorides of Copper, Lead, Iron, Zinc, Tin, and Bismuth, and the Combining Power of the Chlorides, Bromides, and Iodides of Copper and Cadmium, and the Sensitiveness of the Solid Solutions to Light.** GOTTFRIED HERRMANN (*Zeitsch. anorg. Chem.*, 1911, 71, 257—302).—The mixtures of chlorides are examined by Tammann's method of thermal analysis, using Jena glass vessels.



Mixtures of lead chloride and cuprous chloride form a simple eutectiferous series, the eutectic point lying at  $281^{\circ}$  and 34%  $\text{Cu}_2\text{Cl}_2$ . Cadmium chloride melts at  $568^{\circ}$ , and the eutectic of lead and cadmium chlorides melts at  $385^{\circ}$  and contains 30%  $\text{CdCl}_2$ . The eutectic point of lead chloride and ferric chloride is at  $178^{\circ}$  and 50%  $\text{FeCl}_3$ . Lead chloride and stannous chloride form a continuous series of solid solutions. The eutectic of cuprous chloride and stannous chloride melts at  $172^{\circ}$  and contains 77.5%  $\text{SnCl}_2$ . Cuprous chloride and zinc chloride form a eutectic melting at  $243^{\circ}$ , containing 90%  $\text{ZnCl}_2$ , solid solutions being formed to a limited extent at both ends of the series. Cuprous chloride and bismuth chloride have a eutectic point at  $190^{\circ}$  and 85%  $\text{BiCl}_3$ . Cuprous chloride and ferric chloride form a compound,



which melts at  $320^{\circ}$ . There are two eutectic points, at  $306^{\circ}$  and  $263^{\circ}$  and 50% and 88%  $\text{FeCl}_3$  respectively. This compound, which crystallises in green needles, may also be obtained with  $8\text{H}_2\text{O}$  by crystallisation from an aqueous solution. The eutectic of zinc chloride and stannous chloride melts at  $171^{\circ}$  and contains 64%  $\text{SnCl}_2$ , and that of bismuth chloride and ferric chloride melts at  $171^{\circ}$  and contains 23%  $\text{FeCl}_3$ . Ferric chloride and zinc chloride form solid solutions to a limited extent at both ends of the series, the eutectic point being at  $214^{\circ}$  and 70%  $\text{ZnCl}_2$ . The eutectic of cadmium chloride and stannous chloride melts at  $229^{\circ}$ , and contains 90%  $\text{SnCl}_2$ , whilst that of cadmium and zinc chlorides practically coincides with pure zinc chloride. Similarly, the eutectic of lead and zinc chlorides is practically pure zinc chloride. Bismuth and zinc chlorides are only partly miscible in the liquid state, but solid solutions are formed to a small extent. The freezing-point curve of mixtures of lead chloride and bismuth chloride has a discontinuity, but it has not been found possible to determine the composition of the compound, which is not formed in aqueous solutions. A similar case is afforded by mixtures of lead and bismuth bromides, the formula of the compound being again unknown. Cuprous chloride and cadmium chloride form a continuous series of solid solutions, the freezing-point curve having a minimum at  $410^{\circ}$  and 20%  $\text{CdCl}_2$ . A thermal effect is observed at lower temperatures, reaching a maximum at  $350^{\circ}$  and 30%  $\text{CdCl}_2$ , indicating the formation of a compound  $2\text{Cu}_2\text{Cl}_2 \cdot \text{CdCl}_2$ . This compound is greyish-blue, and is not obtained in the wet way. Its formation from the solid solution is promoted by the action of light. Cuprous bromide and cadmium bromide form solid solutions up to 66%  $\text{CdBr}_2$ , at which composition there is a eutectic point at  $420^{\circ}$ . Cuprous bromide undergoes a transformation at  $394^{\circ}$ , and a compound,  $\text{Cu}_2\text{Br}_2 \cdot 2\text{CdBr}_2$ , is formed in the solid state.

Cuprous iodide and cadmium iodide melt at  $606.5^{\circ}$  and  $392.4^{\circ}$  respectively. They form a single series of solid solutions, with a minimum in the freezing-point curve at  $350^{\circ}$  and 90%  $\text{CdI}_2$ . The transformation temperature of cuprous iodide is at  $414^{\circ}$ , and is lowered by addition of cadmium iodide.

Tammann's first rule, that metals of the same natural group do not form compounds with one another, applies also to the chlorides, but the second rule, that a given element forms compounds either with all the members of a natural group or with none, does not apply.

When a pure chloride shows a tendency to undercooling, this tendency is also observed in its mixtures with other chlorides.

C. H. D.

**Thallous Hydroxide.** FRITZ BAHR (*Zeitsch. anorg. Chem.*, 1911, 71, 79—95).—Solutions of thallous hydroxide rapidly attack glass and absorb both carbon dioxide and oxygen. The salt is best prepared by shaking fine turnings of thallium with cold water in a special apparatus, through which oxygen is passed. When the saturated solution is further shaken, yellow crystals of thallous hydroxide separate, and further crystals are obtained by evaporation in a vacuum desiccator over potassium hydroxide. The crystals are then collected by means of a special filter in an atmosphere of hydrogen, washed with ice-cold water and alcohol, and dried in hydrogen. The product is free from lead, but must be freshly prepared for each experiment.

Thallous oxide is obtained by heating the hydroxide momentarily to 150—200° in nitrogen. The solubilities of thallous oxide and hydroxide in water between 0° and 100° are identical. Measurements of the dissociation pressure show that the dissociation temperature  $2\text{TlOH} = \text{Tl}_2\text{O} + \text{H}_2\text{O}$  is 139°, the value 78°, calculated from the heat of reaction, being too low.

Thallous hydroxide is darkened by light in a vacuum, but it has not been found possible to determine the nature of the reaction. Thallous lead sulphate is much less soluble than lead sulphate.

C. H. D.

**The Extraction of Gas from Copper Heated in a Vacuum.** MARCEL GUICHARD (*Compt. rend.*, 1911, 153, 104—107).—When copper is heated at 600—630° in a vacuum, gas is liberated. The rate of liberation gradually decreases, to remain constant when the heating is considerably prolonged (15—20 hours) and the copper has a relatively large surface. When the surface is relatively small, the evolution of gas soon becomes infinitesimal, but if the copper is allowed to cool for several hours and then re-heated, a renewed evolution of gas takes place, finally decreasing to nil. This sequence of phenomena may be repeated several times, and is due to the slow diffusion of gas from the interior to the exterior layers of the copper, as may be shown by heating copper until the evolution of gas has become very small, removing the outer layer with a file and emery paper, and re-heating; an immediate increased evolution of gas takes place.

For the same weight of copper, the greater the surface the greater is the volume of gas liberated in a given time, whereas with the same surface less gas is liberated from fine wire than from larger rods.

The composition of the gas, expressed in terms of 1 c.c., evolved in different cases is as follows:

	CO <sub>2</sub> .	CO.	H + N.	H.
Wire, 0.1 mm. in diameter .....	0.62	0.00	0.38	—
" 0.8 " " .....	0.75	0.12	0.12	—
Electrolytic copper (rods) .....	0.33	0.09	0.57	—
" " fused at 1200° .....	0.6	0.1	—	0.28

T. S. P.

**Binary System Cuprous Bromide-Potassium Bromide.** PIRENO DE CUSARI (*Ann. R. Acad. Lincei*, 1911, [6], 20, i, 749—751).

The author has carried out the thermal analysis of this system with the same experimental arrangements as were employed by him for that of the binary mixtures of cuprous chloride and potassium, sodium, and silver chlorides (this vol., ii, 606). From 730°, the m. p. of potassium bromide, the m. p. of mixtures falls to a minimum at 183°, then rises to 480°, the m. p. of cuprous bromide. At 384° is situated the transition point of two forms of cuprous bromide. At 234° a new solid phase appears, which has the composition  $\text{CuBr}_2\text{KBr}$ , similar to that of the corresponding chlorides.

R. V. S.

**The Action of Alkyl Iodides on Copper Oxide.** HENRY G. DENHAM (*Zeitsch. anorg. Chem.*, 1911, 71, 303—304).—In an attempt to prepare cupric iodide,  $\text{CuI}_2$ , carbon dioxide and methyl iodide vapour were passed over copper oxide at 310°. Cuprous oxide and gaseous products were obtained, but not free iodine.

C. H. D.

**The Action of Ammonia on Mercurous Nitrate.** HARIDAS SAHA and KUMUD NATH CHOUDHURI (*Zeitsch. anorg. Chem.*, 1911, 71, 309—312).—Mercurous nitrate and concentrated ammonia react together, and the filtrate from the black precipitate, evaporated in a vacuum over concentrated sulphuric acid, yields a white powder, having the empirical composition  $\text{Hg}_2\text{N}_2\text{H}_4\text{O}_6$ . This compound, mixed with metallic mercury, constitutes the black precipitate.

C. H. D.

**Aluminium Sulphide.** WILHELM BILTZ and FRITZ CASPARI (*Zeitsch. anorg. Chem.*, 1911, 71, 182—197).—Aluminium sulphide may be prepared by mixing aluminium powder and sulphur in a fire-clay crucible, heating to fusion, cooling, and igniting by means of Goldschmidt's ignition powder. The reaction is very violent, and the product is crystalline. It may be purified by sublimation in a vacuum at 1100—1250°, and then forms white needles resembling asbestos. Good crystals are obtained by sublimation in nitrogen under atmospheric pressure from a carbon tube at 1500—1600°. A yellow sublimate, containing silicon sulphide, is also obtained, this being more volatile than aluminium sulphide.

The sulphide is readily hydrolysed by moisture, intermediate compounds being probably formed. The product obtained by the prolonged action of moist hydrogen sulphide has a composition corresponding with the formula  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O} \cdot \text{Al}_2\text{S}_3$ .

Aluminium sulphide forms long, apparently hexagonal needles,  $D_4 = 3.02$ , and melts at  $1100 \pm 10^\circ$ . Mixtures with aluminium oxide melt at a lower temperature, solid solutions being formed, confirming the partial isomorphism of the oxide and sulphide. Extrapolation of the freezing-point curve gives  $1095^\circ$  as the melting point of aluminium sulphide.

Indications having been observed that aluminium monosulphide,  $\text{AlS}$ , is also formed in small quantity (compare Regelsberger, *Zeitsch. Elektrochem.*, 1898, 4, 547), this compound has been prepared by heating the sesquisulphide to  $2100^\circ$ . A non-

volatile residues thus obtained containing carbide and 12% of the monosulphide, which yields hydrogen with acids according to the equation:  $2\text{AlS} + 6\text{HCl} = 2\text{AlCl}_3 + 2\text{H}_2\text{S} + \text{H}_2$ . The hydrogen evolved is estimated in presence of the methane derived from the carbide by Brück's colloidal palladium method (this vol., ii, 149).

C. H. D.

**The Corrosion and Preservation of Iron.** J. NEWTON FRIEND (*J. Iron and Steel Inst.*, 1911, Reprint 1—65).—The corrosion of iron by air and liquid water containing traces of an acid is relatively less with large than with small areas of iron, the corrosion being greatest at the periphery. It increases with the quantity of dissolved oxygen and with the illumination, hence the corrosion of columns and plates immersed in water is greatest near to the surface. The presence of previously-formed rust accelerates corrosion.

Experiments with Kahlbaum's iron foil show that rusting is completely inhibited by chromic acid above a limiting concentration; in the case examined, 0.111 gram per litre when oxygen is bubbled through the corrosion vessel. Concentrated solutions of chromic acid exert a solvent action on iron. Very dilute solutions of alkali hydroxides suffice to prevent rusting, but the presence of alkali hydroxide, together with salts, such as potassium chloride, only inhibits rusting when above a certain concentration. It is therefore possible for rusting to take place in an alkaline solution. Dilute solutions of neutral salts accelerate corrosion, but concentrated solutions retard it, owing to the diminished solubility of oxygen. The action of acids on iron is not comparable with ordinary corrosion, so that acid "accelerated" tests cannot be employed to determine the resistance of iron or steel to rusting.

The solvent action of drying oils on iron is very small. C. H. D.

**Chromium Steels.** A. PORTEVIN (*Compt. rend.*, 1911, 153, 64—66. Compare Guillet, Abstr., 1904, ii, 739).—The martensite structure shown by steels containing 0.1% of carbon and 7—22% of chromium can be made to disappear by annealing for a sufficient length of time. The product resembles an ordinary moderately hard steel, and shows grains analogous to ferrite, traversed by filaments of a carbide. The paper is illustrated by two micro-photographs. W. O. W.

**Iron Rust.** EDUARD DONATH and A. INDRA (*Chem. Zeit.*, 1911, 35, 773).—The following analyses of different specimens of iron rust are given. *A* is from a steel bomb used for liquid sulphur dioxide, and had thus been exposed for a long time to sulphur dioxide gas. *B* is from a steam boiler, *C* from the base of some machinery, and *D* is wire rust:

	Moisture.	Combined H <sub>2</sub> O.	CO <sub>2</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>2</sub>	NH <sub>3</sub>	FeO.	Fe <sub>2</sub> O <sub>3</sub>	Mn <sub>2</sub> O <sub>3</sub>	Graphite.
A.	4.41	12.21	0.83	0.49	0.46	2.72	1.07	2.23	74.52	0.23	!
B.	1.74	7.63	0.25	0.46	0.08	0.06	0.02	2.79	86.45	0.33	!
C.	2.35	6.23	0.65	3.32	0.43	0.18	0.06	6.04	78.56	1.69	0.49
D.	1.30	1.65	0.93	0.84	0.23	0.07	0.02	1.03	92.94	0.41	!

The authors are of the opinion that some sulphuric acid will always

be found in ordinary rust, and that carbonic acid plays some part in the process of rusting.

T. S. P.

**The Dihydrate of Uranic Oxide.** WILLIAM ORCHESNER DE CONINCK and A. RAYNAUD (*Compt. rend.*, 1911, 153, 63—64. Compare this vol., ii, 403, 496).—Five experiments gave a mean value of 270.46 for the molecular weight of uranous oxide when determined by igniting the hydrate,  $\text{UO}_2 \cdot 2\text{H}_2\text{O}$ , in a current of hydrogen.

W. O. W.

**Thorium Carbonates.** ÉDOUARD CHAUVENET (*Compt. rend.*, 1911, 153, 66—68).—Thorium oxide absorbs carbon dioxide with formation of orthocarbonates. Under ordinary pressure the hydroxide absorbs the gas until the product has the composition  $2\text{Th}(\text{OH})_4 \cdot \text{CO}_2$ . Under 30—40 atmospheres, more gas is absorbed until the normal carbonate  $\text{ThCO}_3 \cdot 2\text{H}_2\text{O}$  is obtained. Under the same conditions the anhydrous oxide, ignited at a temperature not exceeding  $430^\circ$  gives a basic carbonate,  $\text{ThCO}_3 \cdot 6\text{ThO}_2$ . The hydrate  $\text{ThCO}_3 \cdot 8\text{H}_2\text{O}$ , prepared by the action of sodium carbonate on a thorium salt in aqueous solution, loses  $6\text{H}_2\text{O}$  when placed in a vacuum. On heating to  $120^\circ$ , it forms the basic salt,  $\text{ThCO}_3 \cdot \text{ThO}_2 \cdot 1.5\text{H}_2\text{O}$ .

W. O. W.

**Bismuth Carbonate.** LUDWIG VANINO (*Pharm. Zentr.-h.*, 1911, 52, 761—762).—In most cases, bismuth carbonate has the composition  $\text{CO}(\text{O} \cdot \text{BiO})_2$ . It is best prepared as follows, by making use of mannitol: a little water is added to 18.2 grams of mannitol and the whole triturated with 48.2 grams of powdered bismuth nitrate, whereby a solution is obtained. To 100 c.c. of this solution at  $0^\circ$  are added 20.7 grams of potassium carbonate dissolved in the minimum quantity of water; when almost all the potassium carbonate has been added, the bismuth carbonate separates as a fine, heavy powder. The precipitate is washed with water, alcohol, and ether, and dried in the air. Ammonium carbonate may be used instead of potassium carbonate.

It is very difficult to wash bismuth carbonate free from alkali, nitrates, or soluble carbonates. Bismuth metahydrate, dissolved in concentrated hydrochloric acid, is not suitable for the preparation of bismuth carbonate.

T. S. P.

**Some Supposed Iridium Chlorides; Condensed Chlorides.** MARCEL DELEPINE (*Compt. rend.*, 1911, 153, 60—63).—By heating the hydrate  $\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$  at different temperatures, a series of condensed chlorides is obtained. That prepared in ordinary air at  $100^\circ$  has the composition  $\text{IrCl}_{3.54} \cdot 1.66\text{HCl} \cdot 4.5\text{H}_2\text{O}$ , and gives a brown solution in water. When prepared in the same way in dry air the substance forms violet solutions, and has the composition  $\text{IrCl}_{3.54} \cdot 0.66\text{HCl} \cdot 1.5\text{H}_2\text{O}$ ; chlorides prepared at higher temperatures are only slowly dissolved by water. The salt  $\text{IrCl}_{3.44} \cdot 4\text{H}_2\text{O}$  described in Wurtz's Dictionary appears to have the composition  $\text{IrCl}_{3.44} \cdot m\text{HCl} \cdot n\text{H}_2\text{O}$ , where  $m$  is less than unity (compare Claus, *J. pr. Chem.*, 1860, 80, 282). This also forms condensed chlorides when heated. The author has been unable to prepare the anhydrous trichloride described by Claus.

W. O. W.

## Mineralogical Chemistry.

**A Hitherto Unrecognised Crystallo-chemical Relation.** FRANZ LOEWINSON-LESSING (*Centr. Min.*, 1911, 440—442).—It has been already remarked that double salts possess a lower degree of symmetry than either of the component salts, and that hydrated salts have lower symmetry than the corresponding anhydrous salts. It is now pointed out that in complex minerals consisting of a combination of a silicate with some other salt, the degree of symmetry is higher than in the corresponding simple silicate. For example, nephelite is hexagonal, whilst in the sodalite group, where this silicate molecule is combined with sodium chloride, etc., the symmetry is cubic. Again, in the tetragonal marialite there is a combination of the albite molecule (itself triclinic) with sodium chloride. A similar relation is shown to hold with helvine, danalite, melinophane, leucophane, melanocerite, etc. L. J. S.

**Eglestonite from San Mateo Co., California.** AUSTIN F. ROGERS (*Amer. J. Sci.*, 1911, [iv], 32, 48—50).—The mineral eglestonite, previously known only from Terlingua, Texas (Abstr., 1904, ii, 46; 1907, ii, 788; 1910, ii, 306), has been found as minute crystals, associated with other mercury minerals, in a siliceous matrix in serpentine near Palo Alto in San Mateo County. The crystals are cubic with a cubic, octahedral, or rhombic-dodecahedral habit; sometimes they are acicular, owing to elongation of the rhombic-dodecahedron in the direction of a cubic axis. Their orange-yellow to brownish-yellow colour is changed to black on exposure to light, but the adamantine lustre is retained. An analysis made on 25 mg. gave Hg 88.00, Cl 7.43%, agreeing with the eglestonite formula  $\text{Hg}_4\text{Cl}_2\text{O}$ . L. J. S.

**Formula of Pearceite and of Polybasite.** FRANK R. VAN HORN (*Amer. J. Sci.*, 1911, [iv], 32, 40—44. Compare this vol., ii, 614).—The formula  $9(\text{Ag}, \text{Cu})_2\text{S}_2\text{Sb}_2\text{S}_3$  given for polybasite by H. Rose in 1829 has always been generally accepted; and Penfield in 1896 described pearceite as a new mineral with the analogous formula  $9(\text{Ag}, \text{Cu})_2\text{S}_2\text{As}_2\text{S}_3$ .

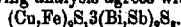
Rammelsberg (*Mineralchemie*, 1875) had, however, suggested the formula  $8(\text{Ag}, \text{Cu})_2\text{S}_2(\text{Sb}, \text{As})_2\text{S}_3$ . A discussion of the published analyses (seven of pearceite and ten of polybasite) leads the author to the conclusion that the latter formula is the correct one. L. J. S.

**Magnesite Deposits of Eichberg on the Semmering Pass:** Eichbergite, a New Sulphantimonite. O. GROSSPIETSCH (*Centr. Min.*, 1911, 433—435).—These magnesite deposits closely resemble those of other Alpine occurrences described by Redlich and Cornu (Abstr., 1909, ii, 410). Associated minerals are dolomite, quartz, talc, rumpfite, iron-pyrites, stibnite, galena, fahlerz, and a new species called eichbergite.

*Reuschite* occurs as finely granular, dirty white to greyish green masses, under the microscope it shows a confused fibrous or sheafy structure; D 2.666. Analysis gave:

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	H <sub>2</sub> O	Total
29.55	35.15	2.61	19.37	13.00	99.68
30.71	38.10	1.88	17.88	11.30	99.77

*Richbergite*.—A single massive fragment was found embedded in magnesite, and coated with green and yellow alteration products. It is iron-grey, and breaks with an irregular fracture. Hardness over 6; D 5.36. The following analysis agrees with the formula:



Cu	Fe	Bi	Sb	S	Total
3.62	1.45	51.53	30.00	12.74	99.34

L. J. S.

**Schaumopal [Float-stone].** OTTO HAUSER (*Centr. Min.*, 1911, 436—438).—The acid vapours (sulphur dioxide) emitted by the Virunga volcanoes in German East Africa, by their action on the lavas (limburgite, basanite, etc.), have given rise to white cellular masses of opaline silica, intermixed with which is some native sulphur. Analyses I and II are of the pure white material, and III of partly decomposed material (dried at 150°).

	S	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>2</sub>	Cl	H <sub>2</sub> O	Total
I	5.73	81.34	2.56	1.27	—	0.41	—	—	—	0.03	trace	8.20	100.24
II	4.52	82.25	2.34	2.08	trace	0.53	trace	—	—	0.21	0.18	7.99	100.00
III	9.30	78.16	3.59	3.99	7.23	0.55	1.29	0.50	trace	0.24	0.01	—	99.86

L. J. S.

**Rare Gases of Thermal Springs and the Information Yielded by Them in Regard to Radioactivity and the Physics of the Earth.** CHARLES MOUREU (*Bull. Soc. chim.*, 1911, [iv], 9, i—xxv).—A lecture delivered to the French Chemical Society, in which the author's results and conclusions on this subject are summarised (compare Abstr., 1909, ii, 363; 1910, ii, 136).

R. V. S.

## Physiological Chemistry.

**The Action of Trypsin on the Different Oxidative Processes in Animal Tissues.** FR. BATTIELLI and (Mlle.) LINA STERN (*Biochem. Zeitsch.*, 1911, 34, 263—274).—The authors have already shown that there are two classes of oxidative processes in the tissues, namely, those which take place in the presence of the intact cell only (the primary respiration, oxidation of citric and succinic acids, etc.), and those which take place in the presence of extracts of tissue. An investiga-

tion on the influence of trypsin, with employment of the same methods and materials used in former investigations, on the two classes of oxidative processes was undertaken. It was found that trypsin has no influence on the oxidative processes of the latter class. On the other hand, it causes a diminution of the oxidative processes of primary respiration, and oxidation by tissues of citric and succinic acids. It has no influence, on the other hand, on the urico- and alcohol-oxydases, at least when the action of the trypsin has exceeded one hour. The authors discuss recent hypotheses on the action of lipoids on oxidative processes. S. B. S.

**The Action of Radium Emanations on Some of the Main Constituents of Normal Blood.** HELEN CHAMBERS and SIDNEY RUSS (*Proc. Roy. Soc.*, 1911, B, 84, 124—136).—Red corpuscles are hemolysed by  $\alpha$ -rays, and oxyhemoglobin is converted into methemoglobin. Leucocytes undergo marked degenerative changes when subjected to  $\alpha$ -rays. During clotting, the leucocytes appear to move away from the  $\alpha$ -radiated region. This is attributed to changes in the surface-tension of blood serum when radiated. The specific properties of opsonin and hemolytic complement are lost when serum is exposed to  $\alpha$ -rays. The progressive changes caused by these rays indicate that opsonin and complement are not identical. The  $\beta$ - and  $\gamma$ -rays yielded negative results in analogous experiments. W. D. H.

**The Interpretation of the Precipitin Reaction.** D. A. WELSH and H. G. CHAPMAN (*J. Roy. Soc. New South Wales*, 1910, 44, 320—333).—Further experimental evidence is given in support of the authors' contention that in the precipitin reaction the main mass of the precipitate is formed by constituents of the anti-serum. W. D. H.

**The Action of Minimal Amounts of Acid on the Blood-Vessels.** CARL SCHWARZ and FRIEDA LEMBERGER (*Pflüger's Archiv*, 1911, 141, 149—170).—From perfusion experiments on the sub-maxillary gland of the cat, separated from the central nervous system, and on the intra-cranial vessels of the dog, it is shown that very dilute acids cause temporary vaso-dilatation. Acids weaker than carbonic, aminopropionic and aminocacetic have, however, no action. This occurs whether the animals have been poisoned with nicotine, and, as in the case of adrenaline, the effect is a peripheral one. The conclusion drawn is that the increased production of carbon dioxide and acid products which accompanies activity is a cause of the dilatation of the vessels of the active organs. W. D. H.

**Action of Pancreatic Lipase.** Contributions to the Biology of Enzymes. SABATO VISCO (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 780—787).—The author has examined the action of pancreatic juice on triolein (sweet almond oil) at 40°, and finds that the amount of fat hydrolysed is increased when a further portion of juice is added to a mixture in which no further hydrolysis is taking place. When, in the same circumstances, more oil is added, the absolute amount of acid



present is also increased to some extent, although not always. The addition of bile to a mixture of fresh juice and oil accelerates the hydrolysis, but does not increase its ultimate amount, but when fresh juice is added repeatedly, the addition of bile does not increase even the velocity of hydrolysis, and appears sometimes to diminish it.

R. V. S.

**The Relationship of Nitrogen and Sulphur in Metabolism.** OSCAR GROSS (*Zeitsch. exp. Path. Ther.*, 1911, 9, Reprint 19 pp.).—The present research arose from the study of certain features of metabolism in alcaptonuria. In dogs fed on horseflesh, the N : S ratio is practically equal in intake and output. In inanition, the nitrogen and sulphur excretion both fall, but the N : S ratio falls also, with certain rises at intervals. In lecithin feeding, although there is again a general correspondence between the ratio in the food and excreta, there is a tendency to nitrogen retention; lecithin is, however, not a protein sparer. The administration of alkalis has no effect on the N : S ratio.

W. D. H.

**The Action of the Enzymes of the Stomach, Pancreas, and Mucous Membrane of the Small Intestine on Gelatin.** D. MINAMI (*Biochem. Zeitsch.*, 1911, 34, 248—260).—By the action of pepsin, hydrochloric acid, and extract of the mucous membrane of the small intestine on gelatin, only a small amount of hydrolysis takes place (determined by Sørensen's titration method). The pancreas extract has a much stronger action, or largely breaks down the peptide bonds. Peptides, which are not precipitated by tannin solutions, appear to be formed, and also small quantities of L-leucine and L-proline. No glycine was found, and in this respect the pancreas gelatinase differs from gelatinase *B. prodigiosus*, by the action of which glycine is formed.

S. B. S.

**The Resorption of Gelatin in the Small Intestine.** D. MINAMI (*Biochem. Zeitsch.*, 1911, 34, 261—262).—Gelatin, undigested and digested with pepsin and pancreatin, was introduced into isolated loops of the small intestine of dogs, and the amount which had been resorbed determined after intervals of one hour by washing out the contents of the loops and estimating the nitrogen. Very little undigested gelatin is resorbed, but larger quantities of the peptonised protein, and still larger quantities of the pancreatised protein, under the above conditions.

S. B. S.

**Fermentation Processes in the Digestive Tract of Ruminants.** I. MARKOFF (*Biochem. Zeitsch.*, 1911, 34, 211—232).—By means of a modified Haldane gas-analysis apparatus, which is figured, estimations of the hydrogen, methane, and carbon dioxide and nitrogen from the paunch and colon of oxen and goats were made. The gases were withdrawn by means of stomach tubes. In the case of the stomach, the quantity of carbon dioxide was sometimes less than that of the methane, and in the maximum, 1.52 times that of the methane. When, however, the stomach contents were removed and

submitted to fermentation *in vitro*, the quantity of carbon dioxide was three to four times that of the methane. This ratio increased on addition to the contents of soluble sugars. The carbon dioxide is apparently, therefore, resorbed as it is formed in the stomach. In the colon, the ratio of carbon dioxide to methane is smaller than in the stomach, being in two cases 0.35 and 0.18 to 1 respectively. The ratio of the methane to hydrogen was large, varying in a large number of experiments between 9.84 and 789:1 in the stomach and 25.8 and 26.8 (in two experiments only):1 in the colon. In the fermentation experiments carried out *in vitro* with the contents of the stomach and colon, the amount of hydrogen could be largely increased by the addition of soluble carbohydrates.

S. B. S.

**The Adaptation Capacity of the Animal Organism to Over-Abundant Nutrient.** E. GRAFE and D. GRAHAM (*Zeitsch. physiol. Chem.*, 1911, 73, 1—67).—In dogs, over-feeding for long periods leads to retention of nitrogen, but the body-weight remains fairly constant. This appears to be due to great activity, increase of oxidation, and loss of water. Full metabolic details are given; the respiratory figures point to the existence of a *luxus consumption*.

W. D. H.

**The Behaviour of Glycogen in the Ovary of *Rana fusca*.** MAX BLEIBTREU (*Pflüger's Archiv*, 1911, 141, 328—342).—The total glycogen in the frog and that of the liver increases from April onwards, reaching its maximum in September and October and diminishing during the winter. The glycogen of the ovary steadily increases from July onwards until the next April, when nearly half the glycogen of the body is contained in the eggs. The results, which on the whole confirm Kato's, point to the importance of glycogen in the nutrition of the eggs.

W. D. H.

**Chemical Composition of Normal Cerebro-spinal Fluid. True Nature of this Liquid.** W. MESTREZAT (*Bull. Soc. chim.*, 1911, [iv], 9, 683—688).—The paper contains the results of the complete analysis of a mixture of twenty normal fluids preserved by heat, and the means of various estimations carried out with about sixty individual fluids. The following physical constants were determined:  $d^{15}_4$  1.00759,  $\alpha$  -0.577°. The composition was found to be as follows (in grams per litre): water, 996.62; total solids, 10.90; ash, 8.86. Analysis of the ash gave the following results (in grams per litre of the original liquid):

Na <sub>2</sub> O.	K <sub>2</sub> O.	CaO.	MgO.	Al <sub>2</sub> O <sub>3</sub> (?).	Fe <sub>2</sub> O <sub>3</sub> .	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	N <sub>2</sub> O <sub>5</sub> .	CO <sub>2</sub> .	Cl.	Loss.
4.346	0.251	0.095	0.050	0.0007	0.002	0.029	0.028	traces	0.550	4.448	0.0023

Normal (as distinct from pathological) cerebro-spinal fluid only contains traces of albumin, and no albumoses or peptones. No diastatic action could be observed. The close resemblance between cerebro-spinal fluid and blood serum is pointed out, and it is shown that the former, as well as the fluids of the eye and of the internal ear, has the composition which would be expected if it had been produced by dialysis of blood serum. This discredits the view that it is a glandular secretion.

R. V. S.

**The Functions of the Liver.** F. WINKEL (*Chem. Zeitsch.*, 1911, 34, 233-241).—The animals employed were geese, and the action of the liver was partly excluded by exposing the portal vein, and severing it between two ligatures. It was found, from analyses of the urine, that considerable quantities of carbohydrate are assimilated, even when the action of the liver is excluded. The organism under these conditions shows a varied tolerance to different sugars, especially to levulose, which is not very markedly different from the tolerance under normal conditions. From these results the conclusion is drawn that in certain diseases of the liver, the diminished tolerance to levulose is not due to injury to the liver parenchyma, so much as to other general disturbed conditions. The exclusion of the liver also causes a marked increase in the ammonia excretion, and, after administration of glycine, the increase of amino-acid excretion is greater when the liver is excluded than in normal animals.

S. B. S.

**The Relation of the Spleen to the Fixation of Antigens and the Production of Immune Substances.** ARNO B. LUCK-HARDT and FRANK C. BECHT (*Amer. J. Physiol.*, 1911, 23, 267-274. Compare this vol., ii, 217).—When an optimum dose of antigen (goat's or rat's blood) is injected intravenously into a dog, the antigen is partly fixed by the spleen; for if the spleen of the dog is removed, emulsified, and introduced into the peritoneal cavity of a normal dog, the specific immune substances appear in the serum of the latter, whereas the introduction of normal spleen produces no such result. The introduction of "immune" heart muscle, liver, bone-marrow, and lymph glands did not give a positive result. Dogs from which the spleen has been removed do not produce hæmolyins, hæmagglutinins, or hæmopsonins as rapidly, nor in so high a concentration, as normal dogs.

W. D. H.

**The Relationship between Muscular Rigor and Protein Coagulation; Chemical Stimulation of Muscle. II. Rigor Produced by Salts.** ERNST ROSSI (*Zeitsch. Biol.*, 1911, 56, 253-273. Compare Abstr., 1910, ii, 730).—If the curarised sartorius of a frog is immersed in thiocyanate solutions it contracts immediately, and after some time becomes quite inactive. The more concentrated the solution, the greater is the initial contraction, which in *N*-solutions becomes partly and in *2N*-solutions a completely permanent rigor. There are slight differences in the action of the potassium and sodium salts. Salicylates act in a similar way. Potassium and sodium iodides also act similarly, but if the muscle is immersed in *2N*-sodium bromide, potassium or sodium chloride solutions, the initial contractions pass off. If the *2N*-sodium and potassium thiocyanate solutions be replaced by the indifferent Göthlin's solution at the commencement of their action, the initial contraction will pass off. If this experiment is repeated, several times, the thiocyanates after a time fail to produce contraction. Thiocyanates and salicylates also gradually destroy the irritability of the muscle to chloroform. *N*- and *2N*-solutions of sodium thiocyanate also produce the rigor contraction when injected into the blood-stream.

S. B. S.

**The Action of Veratrine on Striated Muscle.** I. G. LANN (*Zeitsch. Biol.*, 1911, 66, 223—252).—The experiments were carried out on the isolated sartorius muscle of a frog, and the contractions recorded after stimulus and after addition of veratrine to the Ringer's fluid in which the muscle was suspended. The critical toxic amount, that is the quantity of poison necessary to cause a submaximal tetanus lasting a few seconds after a response to a momentary stimulus, was determined under different conditions of temperature, changes in the concentration of the salts in Ringer's fluid, etc. The tetanus is assumed to be due to the effect of the interaction of the metabolism products and the poison. The most noteworthy effect due to the alteration of the contents of the fluid in which the muscle is suspended is that resulting from the change in the calcium content. Diminution in calcium content increases the sensitiveness of the muscle to the poison, whereas an increase diminishes the sensitiveness.

S. B. S.

**Biochemistry of Protozoa.** THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1911, 73, 109—127).—Masses of *Goussia Gadi* removed from the swim-bladders of various sea-fish contained 14% solids, 12.9% organic matter, and 1.25% nitrogen. Considerable quantities of cholesterol were separated out, but no chitin or other carbohydrate-like substance. Among the proteins a phosphorus-free glucoprotein and a gelatin-yielding material were identified, with traces of a substance resembling elastin, and from the sporozoites, proteoses.

W. D. H.

**Acapnia and Glycosuria.** YANDELL HENDERSON and FRANK P. UNDERHILL (*Amer. J. Physiol.*, 1911, 28, 275—289).—Acapnia (diminution of carbon dioxide in the body) is a frequent concomitant of hyperglycæmia and of glycosuria. In some experimental forms of diabetes, prevention of acapnia obviates disturbances of the sugar-regulating functions. Traumatic and emotional glycosuria, and that produced by etherisation are believed usually to be due to acapnia. Injection of "peptone" is well known to cause acapnia (Lahousse, 1889); it is now found that it also leads to hyperglycæmia. In diabetic coma, an acute and true acapnia occurs as a result of hyperpncea, and not merely due to the expulsion of carbon dioxide from the blood by acids; for in acidosis the acidity (H ion concentration) is probably below the normal, and the hyperpncea is induced by the ethereal (not the acid) acidosis substances, for instance, acetone. The only certain criterion of acapnia or hypercapnia is analysis of the alveolar and blood gases.

W. D. H.

**The Composition of Human Milk in Nephritis.** ST. ENGEL and HANS MÜRSCHHAUSER (*Zeitsch. physiol. Chem.*, 1911, 73, 101—108).—In nephritis, the residual nitrogen of both blood and milk is increased, but on the whole the secretion and composition of the milk are but little altered. The mammary gland can act as an excretory organ for urinary constituents, but neither mother nor child suffers.

W. D. H.

**Anæsthetics.** AUGUSTUS D. WALLER, FREDERICK W. HEWITT, BLUMFELD, JOHN A. GARDNER, and GEORGE A. BUCKMASTER (*Brit. Assoc. Report*, 1910, 268—281).—This report deals with the principles of anæsthesia by ether vapour [Waller], the rate of assumption of chloroform by the blood and the percentages of chloroform found in the blood of cats at the asphyxial point, using different strengths of chloroform-air mixture [Buckmaster and Gardner], and the influence of oxygen on the anæsthetic effect of chloroform [Hewitt and Waller].

T. S. P.

**Glycogenic Property of Glucosamine.** F. ROGOZIUSKI (*Compt. rend.*, 1911, 153, 211—213).—Glucosamine is an important constituent of many proteins. Several investigators have experimented with rabbits to ascertain whether the introduction of glucosamine, as such or as a derivative, increases the amount of glycogen; the results, however, have all been negative. The author has experimented on a young chicken, four days old, but here again, after the introduction of glucosamine hydrochloride through the stomach, the amounts of glycogen in the liver and in the muscles are not greater than the customary amounts in chicken of this age.

Comparative experiments have been made on the behaviour of an emulsion of yeast (freed from glycogen) on distilled water, 1% aqueous sucrose, 1% aqueous glucosamine acetate, and 1% aqueous isoglucosamine acetate. Fermentation commenced at once in the sugar solution, and after four hours the presence of glycogen was detected by the coloration with iodine. The solutions of glucosamine and isoglucosamine, however, did not ferment, and glycogen could not be detected, the microscopic aspects of the two cultures being exactly like that in the distilled water.

C. S.

**Phloridzin- and Phloretin-glycuronic Acids.** I. JOE SCHÜLLER (*Zeitsch. Biol.*, 1911, 56, 274—308).—Investigations were carried out with the object of determining the fate of phloridzin injected into the organism, and for this purpose experiments were undertaken with the object of quantitatively isolating phloridzin or a derivative from the urine. It was found incidentally that when this substance is treated with bromine, it undergoes hydrolysis in addition to bromination, and yields quantitatively the theoretical amount of dextrose, together with tetrabromophloretin. If the bromination is carried out in methyl alcohol instead of water, the methyl glucoside is obtained instead of dextrose. Other glucosides, such as arbutin, undergo a similar hydrolysis on treatment with bromine, whereas others, such as aesculin, quercitrin, etc., yield no free sugar on similar treatment. In the urine of animals treated with phloridzin, more reducing substance is set free than can be accounted for by phloridzin itself, and the author has shown that this is due to the fact that the glucoside is excreted in the form of its glycuronic acid,  $C_{27}H_{33}O_{10}$  which has  $[\alpha]_D - 102.2^\circ$ . The substance is easily soluble in hot water, alcohol, or acetone, but sparingly so in ether, or ethyl acetate. On hydrolysis with dilute sulphuric acid under certain conditions, there is scission of the glucose, and not the glycuronic

group from this substance of conjugated nature. As a result of this action, phloridizinglycuronic acid, which begins to decompose between  $110^{\circ}$  and  $120^{\circ}$ , is obtained; this decomposes on treatment with bromine, yielding tetrabromophloretin and glycuronic acid. The author discusses the older theories as to the formation of glycuronates in view of these results, and draws the conclusion that it is possible that dextrose is first oxidised to glycuronic acid before pairing with the infected substance takes place. He shows, furthermore, that phloridizinglycuronic acid is practically non-toxic, causing no glycosuria in rabbits, and only relatively little glycosuria in dogs as compared with the effect of the free phloridzin. S. B. S.

**The Influence of Urea on the Blood and Milk of Suckling Women.** ST. ENGEL and HANS MÜRSCHHAUSER (*Zeitsch. physiol. Chem.*, 1911, 73, 131—137).—The administration of urea leads to an increase of the residual nitrogen both in the blood and milk of suckling women. W. D. H.

**Oil of Phosphorus and its Combinations in the Organism Investigated by means of the Electroscopic Detection of Phosphorus.** H. SCHMIDT (*Biochem. Zeitsch.*, 1911, 34, 280—305).—The experiments were carried out by means of a modification of Elster and Geitel's electroscope. It was found that phosphorus, even in solution in oil, made the air a conductor of electricity, the effect being proportional to the amount of phosphorus. The temperature optimum was  $60^{\circ}$ . The ionisation diminishes as the oxidation of the phosphorus proceeds; as in oily solutions, a protective layer of insoluble oxides is formed. Inactive gases, such as hydrogen, carbon dioxide, etc., can become saturated with phosphorus vapour, and can then cause the air, as soon as oxidation commences, to become ionised. Pure oxygen can also be saturated with phosphorus vapour, and oxidises only on dilution, when ionisation commences. Phosphorus, in oily solutions, enters into combination with both arterial and venous blood, but not with serum. Elementary phosphorus can be detected in the expired air from animals poisoned by this substance. The air expired from animals, after large intra-arterial doses of phosphorus, is ionised. In such cases, elementary phosphorus passes from the blood to the alveolar wall, where it is oxidised. S. B. S.

**Experimental Poisoning by Oxalic Acid. Localisation of the Poison in the Various Organs.** SARVONAT and ROUBIER (*Ann. Chim. anal.*, 1911, 16, 256—258).—To a dog weighing 18 kilos. were administered increasing doses of sodium oxalate, until after fourteen days 50.4 grams had been given; the last few days the animal suffered from diarrhoea with hæmorrhage, and seemed disgusted with its food, so that it did not take the full dose given. The dog was then killed by severing the femoral vein, and the organism washed out by injection with physiological salt solution. The various organs were, including the blood, then examined for oxalic acid.

The blood showed 0.0017%, a portion of the liver 0.0098%, two lungs 0.0106%, two kidneys 0.0225%, a portion of the sinews 0.0250%, and the brain 0.0270% of oxalic acid. L. DE K.

**Forensic Detection of Veronal.** L. V. HAMBURSKA (*Arch. Pharm.*, 1911, 249-252).—The examination, almost immediately after death, of the body of a woman killed by veronal, showed the presence of only extremely small quantities of the poison in the urine, spleen, heart, liver, bile, oesophagus, stomach, and intestines. The author points out that this is a case where the greater part of the poison must have been eliminated from the system before death occurred. C. S.

**Influence of Oxidation on the Toxicity of Urohypotensine.** J. E. ABELOUS and E. BARDIER (*Compt. rend.*, 1911, 153, 122-123).—Urohypotensine has been oxidised at 40° for two hours by sodium permanganate, persulphate, and chlorate respectively. On rabbits, 0.03 gram of urohypotensine per kilo. of body-weight is never a lethal dose, but the injection of the oxidised toxin into the blood stream causes death almost instantly. Sodium chlorate is the best oxidising agent, in that its effects are constant and regular.

At present little can be said regarding the nature of the oxidised urohypotensine. Possibly very toxic nitriles are produced, because agents, such as sodium thiosulphate, which are antitoxic to certain nitriles show a similar behaviour towards oxidised urohypotensine. C. S.

## Chemistry of Vegetable Physiology and Agriculture.

**The Mechanism of Alcoholic Fermentation.** ALEXANDRE LEBEDEF (Compt. rend., 1911, 152, 136-139. Compare Abstr., 1910, i, 706).—From the analysis of the *p*-bromophenylhydrazone of hexosephosphoric acid which he has now succeeded in recrystallising, the author concludes that hexosephosphoric acid has the composition previously ascribed to it by Young (Abstr., 1910, i, 12). Extract of dried yeast is stated to ferment a 5% solution of dihydroxyacetone as readily as saccharose. When the fermentation takes place in presence of phosphate, an organic compound is obtained which is identical with the hexosephosphate produced from a hexose under similar conditions. A theory of the alcoholic fermentation of sugar is given, according to which in the presence of the enzyme the hexose is first converted into two molecules of a triose; these then condense with the phosphate to form triose-phosphate, and this polymerises to form a hexosephosphate, which then reacts with water with production of carbon dioxide, alcohol, and free phosphate. W. J. Y.

**The Reduction of Furfuraldehyde by Yeasts During Alcoholic Fermentation.** CARL J. LINTNER and H. J. VON LANGE (*Zeitsch. physiol. Chem.*, 1911, 72, 449-454).—The disappearance of furfuraldehyde in yeast cultures is due to its reduction to furfuryl alcohol, and not to its oxidation to pyromucic acid. This

change is not influenced by yeast suspended in water, but the rate of change is not so great as in the case of fermenting yeast.

Under favourable conditions about 70% of the furfuraldehyde supplied is converted into a mixture of two parts of furfuryl alcohol and one part of a crystalline substance which has not been identified. This substance appears to be related to furfuryl alcohol, and is probably produced by secondary action. An experiment, in which 20 grams of furfuraldehyde were added to 4 litres of 10% sucrose solution and 200 grams of carefully washed bottom yeast, after incubation at 18–20° for four days, gave 4 grams of furfuryl alcohol, b. p. 166–170° (uncorr.)/720–730 mm. For identification, furfuryl diphenylcarbamate was prepared according to Erdmann's method (Abstr., 1902, i, 553).

H. B. H.

**The Behaviour of Yeast Enzymes when Free and United to Protoplasm.** HANS EULER and SIXTEN KULLBERG (*Zeitsch. physiol. Chem.*, 1911, 73, 85–100).—Details are given of the action of various antiseptics, anaesthetics, and drying on the activity of the maltase, invertase, and zymase of yeast. The enzymes are believed to be original constituents of the plasma, and are separated in the living cell from the plasma, and again regenerated there; they are then easily extracted, and are present in relatively large quantities; or the separation may be produced partly by drying the cells or by mechanical means, which lead to the death of the plasma. Towards antiseptics they are comparatively insusceptible when freed from the living plasma.

W. D. H.

**Electromotive Phenomena in Plants.** AUGUSTUS D. WALLER, (Mrs.) A. M. WALLER, F. GOTCH, J. B. FARMER, VICTOR H. VELEY, and F. O'B. ELLISON (*Brit. Assoc. Reports*, 1910, 281–290).—This report deals with the rate of intoxication and temperature, the evolution of hydrocyanic acid by laurel leaves, protoplasm and water, and a new method for the quantitative estimation of hydrocyanic acid (compare Waller, Abstr., 1910, ii, 759). There is an appendix on the blaze currents of laurel leaves in relation to their evolution of hydrocyanic acid [(Mrs.) A. M. Waller].

T. S. P.

**Mechanism of Carbon Assimilation.** III. FRANCIS L. USHER and J. H. PRIESTLEY (*Proc. Roy. Soc.*, 1911, B, 84, 101–112).—The catalase enzyme is not exclusively localised in the chloroplasts, as previously stated; subsequent experiments merely indicated that it is more concentrated in the green residue obtained when the juice of crushed leaves is filtered than in the filtrate.

Evidence is given that the primary products of the photolysis of aqueous carbon dioxide are formaldehyde and hydrogen peroxide, and that the evolution of oxygen is due to the decomposition of the hydrogen peroxide by catalase. Up to this point the process is, therefore, non-vital.

N. H. J. M.

**Composition of the Plasma Membrane.** W. W. LEFESCHKIN (*Ber. Deutsch. Bot. Ges.*, 1911, 29, 247–261).—The colloidal solution



of plasma membrane (*ibid.*, 1910, 28) contain oily substances in addition to water and proteins. It is uncertain whether it contains a mixture of lecithin and cholesterol, as assumed by Overton.

N. H. J. M.

**Increased Rate of Diffusion of Dextrose.** S. RYWSOCH (*Ber. Deut. bot. Ges.*, 1911, 29, 204—210).—Dextrose in 2% solutions containing 2% of sucrose was found to diffuse more quickly than in absence of sucrose. The conclusion is drawn that the migration of substances in plants is mainly due to diffusion and that diffusion is assisted by the presence of two or more kinds of sugars.

N. H. J. M.

**The Behaviour of Green Plants towards Gaseous Formaldehyde.** VICTOR GRAPE (*Ber. Deut. bot. Ges.*, 1911, 29, 19—26. Compare Abstr., 1909, ii, 922; 1910, ii, 335).—Experiments with *Phaseolus vulgaris*, in which the above-ground portions were supplied with formaldehyde in the form of vapour, showed that the production of starch is hindered by formaldehyde, and that the plants contained more than twice as much reducing sugar as similar plants grown under normal conditions.

Acetaldehyde (10 c.c. of a 0.5% solution) and benzaldehyde (20 c.c.) checked the growth of the plants more or less completely. Acetic acid is more active than acetaldehyde, whilst benzoic acid had no appreciable effect.

N. H. J. M.

**Direct Guaiacum Reaction Given by Plant Extracts.** (Miss) M. WHELDALE (*Proc. Roy. Soc.*, 1911, B, 84, 121—124).—Catechol can be detected with ferric chloride in extracts of plants which give the direct action and a brown pigment when exposed to chloroform vapour. It was not found in any appreciable quantity in plants giving the indirect action only.

A slightly alkaline solution of catechol which has developed a brown colour by exposure to air produces a blue coloration when added to a peroxydase solution and guaiacum tincture. Similar experiments with phenol, resorcinol, quinol, pyrogallol, phloroglucinol, with benzoic, salicylic, *m*-hydroxybenzoic, *p*-hydroxybenzoic, protocatechuic, gallic, and tannic acids, and quercetin gave negative results.

The conclusion is drawn that the direct action given by extracts of the plants examined is due to the presence of catechol.

N. H. J. M.

**The Localisation of Betaine in Plants.** VLADIMIR STANKE (*Zeitsch. physiol. Chem.*, 1911, 72, 402—409. Compare Abstr., 1910, ii, 336).—The method of isolating betaine from plants is described. Analyses of the different parts of *Beta vulg. sacchar.*, *Triticum vulgare*, *Lycium barbarum*, *Atriplex canescens*, and *Amaranthus retrofractus*, indicate an irregular localisation of the compound. The highest percentages are found in the leaf, with a gradual decrease from the early stages of growth to dead ripeness. Young shoots are also rich in betaine, whilst the bark and wood (*Lycium* and *Atriplex*) contain very little. The root and leaves of *Amaranthus* contain 0.48% and 2.16%

respectively, and those of the sugar beet 0.95—1.20% and 2.62% betaine. The seeds of all the plants tested were strikingly poor in this compound. The whole of the analyses appear to indicate a localisation of betaine at points of energetic physiological activity. The high percentages found in young leaves, shoots, and the root of a biennial plant such as sugar-beet lead to the conclusion that betaine plays an important part in the nitrogen metabolism of plants, but does not serve as reserve food-stuff.

H. B. H.

**Relation of the Odorous Constituents of Certain Plants to Plant Metabolism.** FRANK RADAK (*J. Amer. Chem. Soc.*, 1911, 33, 1242—1247).—From experiments on the Canada fleabane (*Erigeron canadensis*), bergamot mint (*Mentha citrata*), peppermint (*Mentha piperita*), and wormwood (*Artemisia absinthium*), the following general statements are made. In every case the plant is distilled with steam, and the essential oil obtained is analysed for its content of esters and alcohols. The esters (which are regarded as the odorous constituents of the plant) do not seem to be affected during the fructification of the plant. The amount of the esters increases very largely during the growth of the plant, the amount after flowering being sometimes two or three times as great as that before flowering; the percentage of alcohols, however, bears a very slight relation to the life processes of the plant. The odorous constituents apparently are simply products of excretion, and are of no further use to the plant. The effects of drying, budding, blossoming, and fruiting on the life processes of the plants have been examined; in every case there is a change in the aromatic constituents, but in no instance has a decided consumption of the ester or alcoholic constituents been observed.

C. S.

**Rôle of Nucleo-proteins in Plants.** W. ZALESKI (*Ber. Deut. bot. Ges.*, 1911, 29, 146—155).—The production of nucleo-proteins takes place in all growing cells; a considerable increase was observed in the growing portions of seedlings of *Zea mays* and in *Vicia faba*. From the results of experiments with different plants, the conclusion is drawn that the nucleo-proteins are formative substances which have a share in the production of protoplast.

N. H. J. M.

**Composition of Various Oleaginous Seeds from French West Africa.** ALEXANDRE HÉBERT (*Bull. Soc. chim.*, 1911, [iv], 9, 662—672).—The paper gives in detail the yield and composition of the fats extracted from the fruits of a number of tropical plants, and the composition and agricultural value of the residual cakes.

*Dumoria Heckelti*.—The adult tree yields per year about 30 kilos. of fat ("Dumoria butter") containing 33% of unsaturated acids (chiefly oleic acid) and 67% of solid acids (apparently stearic, palmitic, carnaubic, and cerotic acids).

*Chrysophyllum africanum* yields but little fatty matter (2% of the fruit). *Chrysophyllum d'Adzopé* and *Omphalocarpum anacanthum* also give only small quantities of oil.

The seeds of *Carapa microcarpa* yield 35% of fat, which consists of olein, stearin, palmitin, and myristin, together with volatile esters.

The oil from *Balanites nana* contains much oleic acid, but the yield does not exceed 2% of the seeds.

*Biomodendron africanum* yields only 8.7% of an oil containing 70% of unsaturated acids (probably oleic and linoleic acids) and 30% of solid acids (probably palmitic and some myristic acid).

*Sacoglottis Gabonensis* gives in very small quantity an oil resembling olive oil, and 5% of a resin can also be obtained from the fruits.

*Pentadesma butyracea* yields a fat known as "Tama butter," which contains 10% of liquid acids (oleic acid) and 90% of solid acids (stearic and palmitic acids).

R. V. S.

**Chemical Examination of Woody Aster.** L. CHARLES RAYFORD (*J. Amer. Chem. Soc.*, 1911, 33, 1189—1195).—The woody aster (genus *Xylorrhiza*), which apparently has been the cause of extensive sheep poisoning in Wyoming for several years past, is being thoroughly examined. The present paper describes the collection of the plant at the flowering season and the preparation of the roots and tops (that is, everything above the surface of the ground) for analysis, the action of various extractives, the proximate analysis of the roots and tops for moisture, ash, fibre, pentosans, proteins, dextrin, and starch, and the analysis of the ash of the tops and of the roots. Alkaloids are not present in the leaf.

C. S.

**Chemical Nature of Organic Nitrogen in the Soil.** S. I. JORDI (*J. Amer. Chem. Soc.*, 1911, 33, 1226—1241).—Practically all of the nitrogen in soils is of an organic nature. Various plots on the Experimental Station on the Wisconsin Drift have been treated with manure, hay, straw, and other materials representing the principal sources for humus formation. After three years, samples of the soils have been examined. After having found that boiling water extracts at most about 8% of the total nitrogen from the soil, the author uses boiling concentrated hydrochloric acid for ten to fifteen hours, or 20% hydrochloric acid for twenty to thirty hours, whereby about 76% of the total nitrogen is extracted. The hydrochloric acid extract is evaporated to dryness, and the residue is distilled with cream of magnesia; the distillate contains, in the form of ammonia, all the nitrogen present as amides in the soil, the amount of nitrogen being from 25.5% to 33% of the nitrogen extracted. The residue from the distillation with the magnesium oxide is extracted with water, and the solution, after being acidified with sulphuric acid, is treated with phosphotungstic acid, whereby the diamino-acids are precipitated, whilst the amino-acids remain in the filtrate. The nitrogen from the diamino-acids and the amino-acids respectively represents 12—13% and 22—56% of the nitrogen extracted. The rest of the nitrogen is present in compounds other than amides or amino-acids. Such nitrogen is present to the extent of 47—60% in soils which have not been recently manured.

C. S.

**Disinfection of Plants.** L. DANESI and M. TOPI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 772—778).—The authors record the results of experiments on the value of the following insecticides in destroying *Phylloxera* in its various stages: (1) water at 55° for five minutes; (2)

solution of sodium sulphate (1%) at 55° for five minutes; (3) a solution of sodium bicarbonate (3%) and black soap (1%) for twelve hours; (4) pyridine vapour (0.05%). The eggs when ready to open were killed by (1), (3), and (4), the duration of exposure in the case of the last named being two hours. The same modes of treatment destroy the root-form of the insect. The action of pyridine vapour on the leaf galls was also examined, and it was found to have no ill effect on the plant itself, even after acting on it for six to eight hours. It destroys the larvæ in the galls after three or four hours, but its action on the eggs in that situation is incomplete.

R. V. S.

**"Sugar Sand" from Maple Sap. Source of Malic Acid**  
 WILLIAM H. WARREN (*J. Amer. Chem. Soc.*, 1911, 33, 1205—1211).—"Sugar sand" or "nitre" is the sandy, insoluble substance deposited during the evaporation of the sap of the sugar-maple tree (*Acer saccharum*). When practically free from sugar, it is a light grey, microcrystalline powder, tasteless, but slightly odorous. Its composition varies slightly in different samples, but on the average it contains  $SiO_2$  7.74,  $P_2O_5$  0.05,  $Fe_2O_3$  0.39, Ca 17.16, Mg 0.03, moisture 2.60, malic acid 51.48, invert sugar 2.31, sucrose 3.46, matter soluble in ether 0.37,  $CO_2$  0.66, extraneous organic matter 2.35, and undetermined substances 11.40% (by difference). To prepare malic acid from the "sand," the best method is first to prepare calcium hydrogen malate, and from this to obtain the malic acid by means of aqueous oxalic acid.  
 C. S.

**Action of Manganese Sulphate on Vegetation.** GIULIO MASONI (*Staz. sper. agrar. ital.*, 1911, 44, 85—112).—Pot experiments in which magnesium and iron sulphates, both separately and together, and sodium sulphate were applied to maize and lupins.

As regards maize, the addition of small amounts of manganese sulphate reduced the amount of dry produce considerably. With the largest amount of manganese sulphate ( $Mn=0.005\%$ ) and iron sulphate in addition, there was a slightly increased production of dry matter, and with iron sulphate alone there was also an increase in dry matter. Sodium sulphate gave nearly the same amount of dry matter as when nothing was added, but greatly increased the amounts of manganese and iron taken up from the soil.

Manganese sulphate alone ( $Mn=0.001\%$ ) increased the dry produce in the case of lupines, and also the percentage of manganese in the dry matter. Manganese sulphate ( $Mn=0.005\%$ ) in conjunction with iron sulphate produces the highest amounts of dry matter (lupines), whilst sodium sulphate also gave an increase in dry matter and an increase of manganese, but not of iron, taken up from the soil.

Manganese sulphate would seem to be injurious rather than beneficial, and any beneficial action is probably due to the acid portion of the salt. Its physiological action is diminished by the presence of iron.  
 N. H. J. M.

## Analytical Chemistry.

**Estimation of Ozone by an Alkaline Solution of Potassium Iodide.** GEDRON LECHNER (*Zeitsch. Elektrochem.*, 1911, 17, 412—414).—The quantity of ozone produced is first found by accurate measurement of the diminution of pressure in the ozoniser. A neutral or an alkaline solution of potassium iodide is then run into the ozoniser; after complete absorption of the ozone, sulphuric acid is added and the iodine titrated; in other experiments the ozone is swept out of the ozoniser by oxygen and bubbled through the potassium iodide solution. In all cases the quantities of ozone found agree very closely with those calculated from the diminution of pressure. The use of an alkaline solution has the advantage that no iodine is set free, and therefore there is no risk of its being carried away with the current of gas.

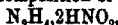
T. E.

**Rapid Estimation of Sulphuric Acid with the Porous Clay Crucible.** FREDERICK KLEIN (*Amer. J. Pharm.*, 1911, 83, 342—346).—The process suited more particularly for the checking of normal sulphuric acid consists in diluting exactly 10 c.c. of the acid with 3 or 4 times its volume of water and heating to boiling. A few c.c. of hydrochloric or nitric acid are added, and then, without interrupting the boiling, 15 c.c. of 10% solution of barium chloride or nitrate. The beaker is then kept hot in a water-bath, and as soon as the barium sulphate has settled completely, it is collected on a specially constructed porous clay crucible of known weight by means of a pump with the so-called carbon filter with rubber stopper, well washed with acidified water until free from chloride or nitrate, dried, heated, and weighed.

A table is annexed facilitating the adjustment of the acid from the result obtained.

L. DE K.

**The Action of Hydrazine Sulphate on Nitrites and a New Method of Estimating Nitrogen in Nitrites.** BIRAN BHABHY DEY, and HEMENDRA KUMAR SEN (*Zeitsch. anorg. Chem.*, 1911, 71, 236—242. Compare Girard and de Saporta, *Abstr.*, 1904, ii, 678).—Solutions of metallic nitrites and hydrazine sulphate react vigorously, even at 0°, the gases evolved containing 2 vols. of nitrous oxide to 1 vol. of nitrogen. The decomposition of hydrazine nitrite,



would yield equal volumes of nitrous oxide and nitrogen, whilst the mononitrite would yield only nitrous oxide and ammonia. The presence of ammonia was confirmed. Amyl nitrite does not react with hydrazine sulphate.

The method may be used to estimate nitrites, the volume of nitrogen, after the removal of nitrous oxide by washing with water, being always two-thirds of that contained in the nitrite.

C. H. D.

**Colorimetric Estimation of Phosphoric Acid.** ISIDORE POUGET and D. GAGOUCHAK (*Bull. Soc. chim.*, 1911, [iv], 9, 649—650. Compare *Abstr.*, 1909, ii, 266).—Further details are given as to the exact mode of working, and the preparation of the necessary reagents.

R. V. S.

**Detection of Perboric Acid and Some Similar Compounds.** WILHELM LENZ and E. RICHTER (*Zeitsch. anal. Chem.*, 1911, 50, 537—544).—Sodium perborate may be readily distinguished from borax by adding to its solution a little potassium dichromate and shaking with ether, which turns blue owing to formation of perchromic acid; the reaction is really due to liberation of hydrogen peroxide from the perborate.

The reaction with potassium iodide is particularly interesting. If to a 1% solution of a per-salt are added 2 drops of 10% solution of potassium iodide, iodine is liberated by ammonium persulphate only. On acidifying with dilute sulphuric acid, iodine is also liberated by ammonium perborate and potassium percarbonate, but not by perchlorate. If potassium bromide is substituted for potassium iodide, no bromine is liberated.

L. DE K.

**Elementary Analysis.** ALBIN KURTENACKER (*Zeitsch. anal. Chem.*, 1911, 50, 548—565).—The author has substituted several metallic oxides for the almost universally used copper oxide in elementary analysis. All combustions were made in a current of mixed air and oxygen or pure oxygen in the usual manner. Instead of the oxidised copper spirals, a boat containing the respective oxides was employed. Special experiments were also made in the case of nitrogenous substances by substituting other metals for metallic copper, in order to reduce nitric oxides formed.

Ferric oxide, obtained by igniting the hydroxide, gives satisfactory results when operating in a current of pure oxygen, but on the whole it is less suitable than copper oxide. Manganese oxide, when obtained by ignition of the nitrate, gives approximate results only; this is chiefly due to the fact that it persistently retains nitrate, which is given off gradually on heating, and renders it unsuitable in the case of nitrogenous compounds. Cobalt oxide obtained from the nitrate, however, is a very suitable oxidiser, and the combustion takes place rapidly, even at a dull red heat. Nickel oxide obtained from the nitrate also gives good results, but it is less suitable than cobalt oxide. Tungstic acid does not cause a complete oxidation, and although with great care fairly satisfactory results are obtained with molybdenum trioxide, its use offers no advantage.

When burning nitrogenous substances, the usual copper spirals may be replaced by a boat filled with porous nickel, prepared by reducing the oxide in a current of hydrogen; nickel spirals proved very unsatisfactory. As, however, metallic nickel slightly reduces carbon dioxide to carbon monoxide, and also slightly liberates hydrogen from water-vapour, the gases must be reoxidised by passing them over red-hot cobalt oxide.

Cobalt cannot be substituted for nickel, as it affects the carbon and hydrogen results.

L. DE K.

**Electro-analysis.** THOMAS M. LOWAY, WILLIAM J. PARK, and HENRY J. SAND (*Brit. Assoc. Reports*, 1910, 79—80).—This report deals with the "electro-deposition of metals" (Park and Hughes, *Abstr.*, 1910, ii, 898), with "apparatus for the rapid electro-analytical separation of metals" (Sand, *Abstr.*, 1910, ii, 66) and the "electro-determination of lead as peroxide" (Sand, *Abstr.*, 1910, ii, 456). Reference is also made to the separation of the four metals, copper, antimony, tin, and lead (Sand, *Proc.*, 1909, 25, 228).

T. S. P.

**Volumetric Estimation of Mercury.** CARL E. SMITH (*Amer. J. Pharm.*, 1911, 83, 311—315).—The methods given in the German Pharmacopœia for the volumetric estimation of mercury in mercuric chloride tablets, ointment of ammoniated mercury, mercuric salicylate, mercury plaster, mercury ointment, and ointment of red mercuric oxide are recommended.

The first three are tested by the iodine titration method, the others by the thiocyanate process.

L. DE K.

**Analysis of Artificial Pearls and Rubies.** RAFAEL CERRERO and ENRIQUE BAYO (*Anal. Fis. Quim.*, 1911, 9, 178—181).—The chemical compositions of the artificial agree with those of the natural gems, excepting that no calcium phosphate is found in artificial pearls. Distinctions between the two kinds are to be made by means of microscopical examination of the structural differences.

G. D. L.

**The Manganese Content of Honeys.** ARTHUR GOTTFRIED (*Pharm. Zentr.-h.*, 1911, 52, 787—788).—The author estimates the manganese in honey as follows: The ash obtained from 25 grams of the sample is dissolved in hot dilute nitric acid and transferred to a 100 c.c. cylinder. After adding some silver nitrate and ammonium persulphate, the solution is warmed and the pink colour developed is matched with a standard permanganate solution.

The amount of manganese seems to bear some kind of relation to the matters precipitable by tannic acid. The average quantity in virgin honeys was found to be 0.04 mg. %; that in commercial samples, 0.065 mg. % of manganese.

L. DE K.

**The Simultaneous Volumetric Estimation of Iron and Vanadium.** ERICH MÜLLER and OTTO DIERFENTHÄLER (*Zeitsch. anorg. Chem.*, 1911, 71, 243—249).—The reduction of vanadium salts by repeated evaporation with hydrochloric acid, conversion into sulphate, and titration with permanganate (Campagne, *Abstr.*, 1903, ii, 761) yields low results with ferro-vanadium. The use of alcohol together with hydrochloric acid reduces the error, without removing it, the results in presence of much iron being too high, owing to the organic compound being retained on evaporation by the large mass of salts. The error is avoided if the evaporation with sulphuric acid is omitted.

One gram of ferro-vanadium is dissolved in concentrated nitric acid, evaporated, and then boiled with hydrochloric

acid and alcohol evaporated to about 5 c.c., and diluted to a known volume. A small part is titrated with permanganate, giving the vanadium. Another portion is used for the iodometric estimation of the iron. The amount of iron found by this method is 0.5% more than that actually present. The iron is more accurately estimated after the titration with permanganate by reducing with sulphur dioxide and titrating the iron and vanadium together with permanganate.

C. H. D.

**Analytical Application of Certain Xanthates.** JAIMÉ FERRER and ANGEL DEL CAMPO (*Anal. Fis. Quim.*, 1911, 9, 173—174).

—Potassium propyl xanthate gives a yellow precipitate with salts of nickel, and a green precipitate with those of cobalt. When a dilute solution of the reagent is used, the nickel is precipitated before the cobalt.

Potassium methyl xanthate is also a delicate reagent for these metals, the nickel salt being soluble and the cobalt salt insoluble in ammonia.

G. D. L.

**Reaction of the Stannous Ion.** JULIO DE GUZMÁN CANANCO (*Anal. Fis. Quim.*, 1911, 9, 177—178).—Stannous chloride yields a carmine-red coloration with ammonium thiocyanate (preferable to the potassium salt) and ammonium molybdate in hydrochloric acid solution in the cold. Excess of hydrochloric acid is to be avoided. The test recognises 0.0001 gram of stannous chloride in 1 c.c., but is given by other reducing agents.

G. D. L.

**The Detection and Estimation of Thorium by means of Iodic Acid.** RICHARD J. MEYER (*Zeitsch. anorg. Chem.*, 1911, 71, 65—69. Compare Meyer and Speter, *Abstr.*, 1910, ii, 459).—Even very small quantities of thorium in mixtures of the rare earths may be readily detected and estimated by means of iodic acid. Two solutions are used: solution I, containing 15 grams of potassium iodate, 50 c.c. of concentrated nitric acid, and 100 c.c. of water; and solution II, 4 grams of potassium iodate, 100 c.c. of dilute nitric acid, D 1.2, and 400 c.c. of water. In making the test, 2 c.c. of the solution to be tested, which must be free from hydrochloric acid, are mixed with 5 c.c. of solution I. Thorium iodate is precipitated together with some iodates of other earths. These are re-dissolved by adding 10 c.c. of solution II and boiling, when the thorium precipitate remains insoluble. About 0.1 gram  $\text{ThO}_2$  per litre may be detected in this way, and the sensitiveness is almost unchanged in the presence even of a large excess of other rare earths. Zirconium is precipitated under the same conditions, but zirconium iodate may be dissolved out by means of oxalic acid. Cerium salts are also precipitated, but may be removed by previous boiling with a little sulphurous acid. The cerous salt is very slowly oxidised by nitric and iodic acids, but this is without influence under the conditions of the experiment.

The separation of thorium and scandium (compare Meyer and Winter, *Abstr.*, 1910, ii, 853) is best accomplished by this method after a double precipitation with ammonium thiosulphate from hydrochloric acid solution, the thorium iodate being decomposed with



ammonia and ignited to oxide. Specimens of orthite from Implak, Finland, examined by this method, gave 0.30%  $\text{Sc}_2\text{O}_3$  and 1.32%  $\text{ThO}_2$  in the fresh mineral, and 1.00%  $\text{Sc}_2\text{O}_3$  and 1.10%  $\text{ThO}_2$  in the weathered mineral. This concentration of scandium in a cerium mineral is purely local, and does not occur in other specimens of orthite.

C. H. D.

**Estimation of Active Hydrogen in Organic Molecules.** BERNARDO ODDO (*Ber.*, 1911, 44, 2043—2052 \*).—The method is based on the interaction of the organic substance and magnesium ethyl iodide in a special weighed apparatus, the loss of weight corresponding with the ethane formed. The apparatus consists of a small flask, *A*, containing the substance dissolved in pyridine, isocamyl ether, toluene, or heavy petroleum. This is connected with a similar flask, *B*, containing magnesium ethyl iodide dissolved in isocamyl ether, into which the delivery tube of the first flask dips. The magnesium ethyl iodide is prepared fresh for each experiment, and contains slightly less than the theoretical quantity of alkyl iodide required by the magnesium taken. A suitable absorption vessel of sulphuric acid is attached to the second flask, and the three are weighed together; the free end is then protected by a calcium chloride tube and a flask of pyrogallol acid.

By suction, air is drawn from *A*, and on release the organo-metallic compound passes over from *B*. Ethane is liberated and escapes from the apparatus, being freed from solvent and moisture in passing out of the apparatus. In pyridine, action takes place at once, and cooling is sometimes necessary; in the other substances it is advisable to warm *A* at 50–60° to complete the reaction. After cooling, the apparatus is re-weighed and the loss determined.

Experiments are quoted for a number of substances showing the number of hydroxyl and active hydrogen groups present.

E. F. A.

**A Reaction for Aromatic Inner Anhydrides Based on the Modification of the Crystalline Form of Iodoform.** BRUNO BARDACH (*Zeitsch. anal. Chem.*, 1911, 50, 545–548).—To the not too strong aqueous solution of the supposed aromatic anhydride (for example, euxanthone or its derivatives), which should be practically neutral and prepared with spring water, is added drop by drop a 2% alcoholic solution of iodoform. If the iodoform separates in delicate needles, inner aromatic anhydrides are present. Albumin, if present, should first be removed.

If, however, the normal hexagonal iodoform crystals are obtained, 3 c.c. of the original solution are mixed with a few drops of Lugol's iodine solution (4 iodine, 6 potassium iodide, 100 of water), and 10 c.c. of ammonia are added. If the solution clears completely, no more iodine should be added. After waiting for an hour and filtering, alcoholic solution of iodoform is added, and a needle-shaped precipitate now points to the presence of aromatic inner anhydrides (such as coumarin) or aromatic hydroxy-acids with a long side-chain or to polyhydroxy-ketones.

L. DE K.

**Estimation of Volatile Fatty Acids** [in Fæces]. F. EDELSTEIN and ERNST WELDE (*Zeitsch. physiol. Chem.*, 1911, 73, 152—156. Compare Welde, *Abstr.*, 1910, ii, 1118).—A reply to McCaughey (this vol., ii, 666). It is shown that when fæces are suspended in water and distilled with phosphoric acid (D 1.12) under reduced pressure, the greater portion of the volatile acids is removed within two hours.  
J. J. S.

**The Titration of Potassium Cyanide in Presence of Potassium Ferrocyanide.** W. D. TREADWELL (*Zeitsch. anorg. Chem.*, 1911, 71, 219—225).—Liebig's method of titrating cyanides in presence of chlorides and thiocyanates fails in presence of ferrocyanides, owing to the solvent action of these salts on silver cyanide, causing the quantity of silver used to be too high. The addition of potassium iodide has been recommended, and is now shown to be satisfactory. The silver solution must be added slowly at the end, as otherwise the precipitate is coarse, and does not redissolve readily. About 0.1 gram of potassium iodide is used in each titration. The results are then quite unchanged by the presence of ferrocyanide.

Electrolytic measurements have also been made, using a concentration cell, the two solutions of which are *N*/10-silver nitrate, and the solution undergoing titration. With pure potassium cyanide, the electrolytic end point coincides with the first appearance of a precipitate. At this point the *E.M.F.* of the cell is 0.500—0.520 volt. Ammonia raises the *E.M.F.* Thiosulphate has a greater disturbing influence than ammonia, but its effect may be greatly lessened by the addition of a larger quantity of potassium iodide as an indicator. Potassium ferrocyanide raises the *E.M.F.*, but not to such an extent that potassium iodide fails to produce a precipitate.  
C. H. D.

**Separation and Estimation of Ammonia and of Pyridine.** MARCEL DELÉPINE and RENÉ SORNET (*Bull. Soc. chim.*, 1911, [iv], 9, 706—710).—The authors employ Gerresheim's method (compare *Abstr.*, 1879, 438; see also Buisson, *Abstr.*, 1907, ii, 306) for precipitating the ammonia from solution in hydrochloric acid by means of mercuric chloride in the presence of sodium carbonate and sodium hydroxide. The pyridine is set free in the filtrate, distilled off, and weighed either as the aurichloride or platinichloride. The ammonia is subsequently liberated from its precipitate by sodium thiosulphate, distilled off, collected in dilute hydrochloric acid, and finally weighed as ammonium chloride.  
W. G.

**Estimation of Nicotine.** GABRIEL BERTRAND and MAURICE JAVILLIER (*Ann. Chim. anal.*, 1911, 16, 251—256).—Twelve grams of the powdered sample of tobacco are boiled in a reflux apparatus with 300 c.c. of 0.3% hydrochloric acid for thirty minutes; when cold, 250 c.c. of the clear liquid or filtrate are taken for analysis. When dealing with *bona fide* tobacco extracts, 5 grams of the sample are diluted to 100 c.c., and 1 c.c. of 10% hydrochloric acid is added.

The solution is now precipitated by adding an excess of 10—20% solution of silicotungstic acid, and after twenty-four hours the precipi-

case is collected and washed with dilute liquid with hydrochloric acid; this operation may be repeated by centrifugal action. The precipitate, which contains all the nicotine, present is then distilled with excess of magnesium oxide; the volatilisation of the alkaloid is much assisted by passing a current of steam, care being taken not to let the contents of the flask get diluted by condensing steam. The distillate is then titrated with standard sulphuric acid with alizarin-sulphonic acid as indicator.

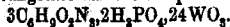
Should the tobacco extracts contain pyridine bases, the results will be vitiated. In this case the titrated liquid is mixed with 1-2% of ammonium chloride, and, after acidifying with hydrochloric acid, reprecipitated with silicotungstic acid. The precipitate after being washed is decomposed by dilute sodium hydroxide, and the nicotine, etc., is removed from the solution by shaking thrice in succession with chloroform; the final volume of the chloroform should be 5 or 10 c.c. This solution is then examined polarimetrically in a 10 or 20 cm. tube. The specific rotatory power of nicotine in a 1 to 2% chloroform solution at 20° is 161.35°. Pyridine bases are optically quite inactive.

If, instead of using sodium hydroxide, the precipitate is treated with ammonia, then, by way of a check, the resulting liquid may, after extraction with chloroform, be evaporated to dryness, and the ignited residue weighed; the weight  $\times 0.1139$  = nicotine. When dealing with unadulterated juices, the volumetric, polarimetric, and ignition results should be practically the same.

L. DE K.

**The Technique of the Phosphotungstic Acid Precipitation.** EKAN WECHSLER (*Zeitsch. physiol. Chem.*, 1911, 73, 138-143).—The solubilities of the phosphotungstates derived from the following bases have been determined. The numbers give the % of substance dissolved by a mixture of four volumes of acetone and three of water: Deuteroalbumose, 2.94; heteroalbumose, 2.24; silk-peptone, readily soluble; *d*-arginine, 120-130; *dl*-arginine, 120-130, *l*-histidine, 160; *d*-lysine, 140; guanidine, 22.8; creatinine, 13.34; guanine, 7.21; adenine, 10.50. Determinations were not possible with methyl-guanidine or phenylalanine. In most cases the mixtures were shaken for an hour before the solubility was determined. The solubility of protalbumose is 0.67 when the precipitation takes place from aqueous solution in the absence of acid, but 6.76 when precipitated in the presence of acid.

Histidine phosphotungstate has the composition



J. J. S.

## General and Physical Chemistry.

**Anomalous Molecular Refraction in the Series of Substituted Glyoximes.** LEO TSCHUGAEFF and P. KOCH (*Compt. rend.*, 1911, 153, 259—261).—The molecular refraction of substituted  $\beta$ - and  $\gamma$ -glyoximes is normal, but is abnormally high in the case of those compounds in which the oximino-groups are in the  $\alpha$ -position relatively to one another. The molecular exaltation is practically constant in the aliphatic series, about 1.3 for the *D*-line, but considerably higher in the aromatic compounds, pyridine solutions of the two benzildioximes showing an exaltation of 3.45. The results of measurements for eight oximes are recorded.

W. O. W.

**Rotatory Dichroism of a Definite Organic Compound (*l*-Bornyl Diphenyldithiourethane).** G. BRUHAT (*Compt. rend.*, 1911, 153, 248—250. Compare Tschugaeff, *Abstr.*, 1910, ii, 812).—The substance occurs in red crystals showing dichroism and anomalous dispersion in toluene solution. When in the superfused condition, it forms a green liquid showing anomalous rotatory dispersion, and measurable circular dichroism. The results of polarimetric measurements are given, and it is shown that the dispersion and dichroism curves are similar, those for the toluene solution being slightly nearer the violet than those for the superfused substance. In both cases Natanson's rule is followed, the rotation being to the left on the red side of the absorption band and to the right on the side towards the violet.

W. O. W.

**The Ultra-violet Spark Spectrum of Air.** FRANZ L. WAGNER (*Zeitsch. wiss. Photochem.*, 1911, 10, 69—89).—Accurate wave-length measurements have been made of the lines in the spark spectrum of air by means of a Rowland concave grating of 6.5 metres radius of curvature and 16,000 lines to the inch. The method used consisted in photographing the spark spectra obtained in air between copper, silver, and aluminium electrodes. The lines common to the three spectra were then sorted out as representing the air lines. In carrying out this process, precautions were taken to ensure that the common lines were not due to the presence of traces of a common impurity in the three metals. In some cases, lines found on only two or even one of the photographic records have for special reasons been adopted as air lines.

The measurements, which extend from  $\lambda = 4146$  to  $\lambda = 2370$ , are given in tabular form and compared with those of previous observers. In the case of each line, the table shows the relative intensity, the particular spark spectra in which it has been observed, and whether the line is due to nitrogen, oxygen, or argon.

As an appendix, the measured lines due to the metals in the three spark spectra are tabulated. These tables have been compared with

the spectra of iron, titanium, vanadium, niobium, and magnesium, manganese, and silicon for the purpose of eliminating lines due to traces of possible impurities. H. M. D.

**Secondary Spectrum of Hydrogen.** O. POINCARÉ and G. NOUZI (*Ann. R. Acad. Lincei*, 1911, [v], 20, i, 819-828).—The authors find that the intensities of the lines in the secondary spectrum of hydrogen are as stated by Hasselberg (compare Dufour, *Abstr.*, 1907, ii, 1). They record in tables the wave-lengths of lines not seen by Watson (*Abstr.*, 1909, ii, 453), and of some lines not mentioned by previous observers, and they have confirmed the existence of certain lines seen only by Watson (*loc. cit.*). R. V. S.

**The Ultra-red Absorption Spectrum of Carbon Dioxide in its Dependence on Pressure and Partial Pressure.** G. HERTZ (*Ber. deut. physikal. Ges.*, 1911, 13, 617-644. Compare von Bahr, *Abstr.*, 1909, ii, 630; 1910, ii, 914).—In reference to Arrhenius's theory that the earth's climate is essentially determined by the absorption of the earth's heat rays by the carbon dioxide and water vapour in the surrounding atmosphere, the author has investigated the absorption of ultra-red rays of wave-length  $\lambda = 14.7\mu$  by carbon dioxide under different conditions.

As found by von Bahr for rays of shorter wave-length, the absorption is not solely determined by the product of the partial pressure and the thickness of the absorbing layer, but is influenced to a large extent by the magnitude of the total pressure. The absorption also differs appreciably according to whether a given value of the total pressure is reached by compressing the pure gas or by mixing it with another gas, such as air or hydrogen. The observations lead to the conclusion that the temperature changes on the earth's surface cannot be attributed to heat ray absorption by the carbon dioxide in the atmosphere.

Absorption measurements were also made with rays in the neighbourhood of  $4.3\mu$  and  $2.7\mu$ . The relationships exhibited in the absorption of these shorter waves appear to be very similar to those found for  $\lambda = 14.7\mu$ . The absorption band at  $\lambda = 2.7\mu$  possesses two maxima, of wave-length  $2.67\mu$  and  $2.75\mu$  respectively.

H. M. D.

**Anode and Cathode Spectra of Various Gases and Vapours.** G. STREAD (*Proc. Roy. Soc.*, 1911, A, 85, 393-401).—A comparison of the two kinds of spectra was effected by means of a discharge tube divided into two halves by an aluminium plate, one side of which formed an anode and the other a cathode. Observations were made with hydrogen, hydrogen chloride, chloroform, carbon tetrachloride, silicon tetrachloride, stannic chloride, benzene, chlorobenzene, carbon disulphide, hydrogen sulphide, sulphur dioxide, hydrogen bromide, hydrogen iodide, ethyl bromide, methyl iodide, cyanogen, and hydrogen cyanide. The general conclusion drawn by the author is that the spectra of electronegative elements tend to appear at the anode, whilst those of electropositive elements show a preference for the cathode. The

differences in the potential gradient and the temperature is supposed to be in some measure responsible for the distribution of the spectra.

In the case of an elementary gas these are probably the chief determining factors, and in the case of hydrogen, which shows the secondary spectrum at the anode and the "four line" spectrum at the cathode, it would appear that a low potential gradient is favourable to the appearance of the secondary spectrum.

H. M. D.

**Measurements in the Silver Spectrum.** FRANZ JOSEPH KASPER (*Zeitsch. wiss. Photochem.*, 1911, 10, 53—62).—Wave-length measurements of the lines in the arc and spark spectra of silver have been made. The arc spectrum measurements are compared with the data of Kayser and Runge and of Exner and Haschek. It has been found that an arc spectrum can be obtained by the employment of silver rods as arc electrodes if the potential and current are suitably adjusted and arrangements are made for the adequate supply of oxygen to the neighbourhood of the electrodes. With an efficient air draught the arc can be maintained continuously for periods of twenty to twenty-five minutes.

H. M. D.

**Photographic-photometric Absorption Measurements of Silver Iodide in the Ultra-violet Spectrum.** CURT SCHELL (*Ann. Physik*, 1911, [iv], 35, 695—726).—A photographic method of measuring the intensity of ultra-violet light is described, and this is applied to the determination of the absorption of ultra-violet light by silver iodide. According to this method, the blackening produced by the light of unknown intensity during a given time is compared photometrically with the effects produced by two beams of known intensity, the blackening produced by one of which is greater and by the other less than that produced by the ultra-violet light of unknown intensity. By this means, measurements of the absorption-coefficient of silver iodide have been made for wave-lengths extending from  $\lambda = 215\mu\mu$  to  $\lambda = 450\mu\mu$ . Chemically prepared silver films, after conversion into the iodide, exhibit the same absorption capacity as those obtained by cathodic pulverisation.

Certain irregularities which are exhibited by the developed photographic plates have been traced to differences in concentration of the developing solution, and it has been found that these can be avoided by previous washing of the plates in water and the employment of slow acting developers.

H. M. D.

**The Band Spectrum of Lead.** HERMANN LAMPRECHT (*Zeitsch. wiss. Photochem.*, 1911, 10, 16—29, 33—52).—Detailed wave-length measurements of the band spectrum of lead have been made, the source of illumination employed being a coal-gas and oxygen blow-pipe flame into which lead chloride was introduced according to Hartley's method. The same spectrum is obtained when the oxide, sulphate, and carbonate are introduced into the flame, but much longer exposures are required than when the chloride is used. The wave-length measurements, expressed in terms of the normal iron lines, are compared with those of Hartley and of Hagenbach and Konen.

By the use of an optical system of greater dispersive power, the constitution of some of the strongest bands has been investigated. The line measurements in four series are in good agreement with the requirements of Deslandres' law, but in other series considerable deviations are found.

H. M. D.

**The Spectrum of Glucinum and its Bands in Different Luminous Sources.** P. E. LECOQ DE BOISBAUDRAN and ANTOINE DE GRAMONT (*Compt. rend.*, 1911, 153, 318—321).—Employing the apparatus previously described (*Ann. Chim. phys.*, 1909, [viii], 17) a new faint band in the indigo has been observed in addition to the two already known in the blue and green. This shows a maximum intensity at  $\lambda$  4709. The wave-lengths and relative intensities of the components of the three bands are recorded. The intensities are considerably increased by employing a spark with self induction up to 0.122 Henry units, when the ultra-violet lines also become perceptible. Strong self induction does not diminish the very sensitive doublet  $\lambda$  3131.2, 3130.5; this also appears in the arc spectrum.

In general there is a striking resemblance between the band spectra of aluminium and glucinum.

W. O. W.

**Influence of Temperature and Magnetisation on Selective Absorption and Fluorescence Spectra.** II. HENRI E. J. G. DU BOIS and G. J. ELIAS (*Ann. Physik.*, 1911, [iv], 35, 617—678. Compare Abstr., 1908, ii, 337, 547).—In continuation of previous measurements, further data relating to the influence of temperature and a magnetic field on the absorption bands of certain substances are recorded. In the case of erbium nitrate and to a less extent ruby, the influence of these factors has been examined in great detail.

H. M. D.

**Fluorescence of the Vapours of the Alkali Metals.** LOUIS DUNOYER (*Compt. rend.*, 1911, 153, 333—336).—The fluorescence of cesium vapour, which from analogy to that of the other alkali metals should be very intense, is found to be too faint at 350° to admit of spectroscopic examination. The green fluorescence of sodium vapour observed by Wood (Abstr., 1908, ii, 150, 546) is due to impurities, for if the metal is pure, the fluorescence is bright yellow and appears at a lower temperature, namely, at about 210°. The purer the metal the more the resonance spectrum is favoured at the expense of that of fluorescence. Potassium vapour commences to be fluorescent at about 215° and is brilliant at 320°.

The fluorescence of rubidium produced by white light is purple-red, and is visible at 180°, but becomes orange at 400°. It appears to be due to two bands, one corresponding with an absorption band and the other appearing at the higher temperature having no obvious relation to absorption.

The polarisation of fluorescence has been studied at different temperatures. The curves connecting partial polarisation and temperature are similar whether the incident light is polarised or not. Rubidium vapour shows maximum fluorescence at 370°, potassium and

sodium at lower temperatures. The cause of depolarisation appears to depend on a mutual action between fluorescing molecules, since polarisation is strongest when the vapour is not saturated, that is, not in contact with an excess of fused metal. W. O. W.

**Fluorescence Absorption and Lambert's Absorption Law in the Case of Fluorescein.** F. KAEMPF (*Physikal. Zeitsch.*, 1911, 12, 761—763).—Experiments have been made to determine whether the fluorescence of fluorescein solutions is accompanied by a special absorption effect. The results obtained with two different forms of apparatus indicate that within the limits of experimental error (5%) there is no special fluorescence absorption, and that the absorption, for different intensities of the incident light, takes place in accordance with Lambert's law. H. M. D.

**Systems of Series in the Spectra of Zinc, Cadmium, and Mercury.** II. FRIEDRICH PASCHEN (*Ann. Physik*, 1911, [iv], 35, 860—880. Compare Abstr., 1910, ii, 3).—Quartz lamps worked with a large current were used in the production of the spectra of the metals, and the influence of a magnetic field on the various lines was investigated in order to throw light on the constitution of the spectra. For zinc and cadmium the data indicate definitely the existence of three systems of series—simple lines, doublets, and triplets. In the case of both metals the triplets appear to be largely combined with the simple lines, but the extent of the combination is much greater for cadmium than for zinc. Mercury also appears to exhibit the same three systems of series, and in this case the combination of triplets with simple lines is extremely large. H. M. D.

**Ultra-violet Radiation from Quartz-mercury Lamps.** VICTOR HENRI (*Compt. rend.*, 1911, 153, 265—267).—The variation in the intensity of the ultra-violet radiation from a quartz-mercury lamp with the strength of the current has been measured by chemical methods. The reactions employed for the purpose include decomposition of dry hydrogen chloride by the rays, decomposition of hydrogen peroxide or of potassium iodide in solution, the appearance of hydrogen ions in a solution of sucrose, the blackening of silver citrate paper, and the sterilising action of the rays on *B. coli*. In the last two cases the radiation increased very rapidly with the current, but the intensity of the rays affecting potassium iodide increased more slowly. A spectrophotometric comparison showed that the extreme ultra-violet radiation increased more rapidly than the total visible radiation from the lamp. W. O. W.

**Influence of Different Physical Conditions on the Ultra-violet Radiations from Quartz-mercury Lamps.** VICTOR HENRI (*Compt. rend.*, 1911, 153, 426—429. Compare preceding abstract).—Employing the silver citrate method mentioned in a previous paper, the intensity of the ultra-violet radiation from a quartz-mercury lamp was measured under different conditions. The radiation is more intense as the temperature of the lamp tube is higher. When burning



in air, the radiation is about fourteen times as intense as when cooled in water. The length of service has but little effect in diminishing the activity of the radiation from a well evacuated lamp.

W. O. W.

**The Grouping of Photochemical Reactions.** FRITZ WIEGERT (*Zeitsch. wiss. Photochem.*, 1911, 10, 1-15).—The characteristics of photochemical reactions are discussed from the point of view of the energy changes which are involved, and a scheme is proposed for the systematic grouping of the different types of change. H. M. D.

**Photochemical Studies. II. The Classification of Light Reactions.** JOH. PLOTNIKOFF (*Zeitsch. physikal. Chem.*, 1911, 77, 472-481. Compare this vol., ii, 452).—A classification of chemical changes influenced by light is represented in tabular form and discussed in detail. The reactions in question are divided into irreversible and reversible changes. There are three main types of irreversible change: (1) May be subdivided into (1a) simple photocatalytic actions, changes which only take place in light and show no after-effect, and (1b) which differs from (1a) inasmuch as the change proceeds in the absence of light. (2) Photochemical catalysis, where the reaction does not proceed either in the presence or absence of light, but when a catalyst is added in small concentration, the change takes place in presence of light, but ceases when the light is withdrawn. (3) Photochemical after-effect differing from (2) inasmuch as the reaction, once started by a catalyst in light, proceeds with the same velocity in the dark. There are two main types of reversible change: (1) in the light a new equilibrium is established; (2) light displaces the equilibrium established in the dark. For details and examples of the different types of change the original paper must be consulted. G. S.

**The Transformation of Energy in Photochemical Reactions in Gases.** EMIL WARBURG (*Sitzungsber. K. Akad. Wiss. Berlin*, 1911, 746-754).—The proportion of absorbed radiant energy which is converted into chemical energy in the decomposition of ammonia under the influence of ultra-violet light has been determined. If  $\alpha$  is the thermal and  $\beta$  the chemical absorption coefficient, the photochemical yield  $s$  is given by the ratio  $s = \beta/\alpha + \beta$ . As the final result of a large number of experiments, it is found that the photochemical yield for the action of rays of wave-length  $\lambda = 0.203\mu$  to  $0.214\mu$  on ammonia at a pressure of 80-90 cms. of mercury is about 2%. There is some evidence of a slight decrease in the yield as the wave-length of the absorbed light diminishes. Since, however, the total absorption coefficient increases considerably with diminishing wave-length, it follows that the chemical absorption coefficient  $\beta$  must also increase with diminishing wave-length within the range of rays investigated.

It is pointed out that the observed small photochemical yield does not really measure the amount of chemical work performed by the absorbed rays for the primary photochemical change,  $\text{NH}_3 = \text{N} + 3\text{H}$ , inasmuch as this is a strongly exothermic reaction,  $2\text{N} + 6\text{H} = \text{N}_2 + 3\text{H}_2$ .

The secondary reaction is quite independent of the light action, but its occurrence continuously results in a diminution of the measured photochemical yield.

H. M. D.

**Measurements of Photochemical Action in Ultra-violet Light by means of Sensitive Films.** CARL SCHALL (*Zeitsch. wiss. Photochem.*, 1911, 10, 89—116. Compare Abstr., 1908, ii, 139; 1909, ii, 359; 1910, ii, 249).—The nature of the photochemical change which gives rise to the coloration of papers impregnated with solutions of diamines under the influence of ultra-violet light is discussed. Measurements have been made which show that the colour change of *p*-phenylenediamine nitrate and of tetrabromoethane, when subjected for a given period to the action of ultra-violet rays, is proportional to the light intensity. A spectroscopic comparison of the active rays in the use of these and other photo-sensitive substances has also been carried out.

H. M. D.

**Photolysis of Alcohols, Acid Anhydrides, Ethers, and Esters by Ultra-violet Light.** DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1911, 153, 383—386. Compare Abstr., 1910, ii, 814; this vol., ii, 86).—A continuation of the previous communication, giving the relative volumes of the gaseous products from a number of substances, principally esters, exposed to light from a quartz-mercury lamp. The gases from alcohol contain 70% of hydrogen by volume; acetaldehyde was detected amongst the products, and formaldehyde recognised in methyl alcohol exposed to the light. Ether gives 14.5 volumes of carbon monoxide and 85.5 volumes of a mixture of hydrogen, methane, and ethane, the latter predominating. Acetic anhydride gives the same gases and also carbon dioxide. Carbon monoxide is the chief product from aliphatic esters. Benzyl formate gives carbon monoxide and dioxide, but ethyl benzoate and salicylate remain unaltered after eight hours' exposure under diminished pressure.

W. O. W.

**Oxidising Action of Dilute Nitric Acid in Sunlight.** ALFRED BENNATH (*J. pr. Chem.*, 1911, [ii], 84, 324—328).—Solutions of acetic, aminoacetic, propionic, butyric, isobutyric, malonic, succinic, and pyrotartaric acids in 2*N*-nitric acid, containing ferric nitrate, acquire a cherry-red colour on exposure to light and continuously evolve a gas, consisting mainly of nitrous oxide together with some carbon dioxide. All the acids yield formaldehyde, which is accompanied, in the case of propionic acid and probably also succinic acid, by acetaldehyde, the latter being produced by the loss of carbon dioxide from the immediately formed pyruvic acid. *iso*Butyric acid yields acetone, which is further oxidised to formaldehyde and acetic acid. With butyric and pyrotartaric acids, the formaldehyde is accompanied by other aldehydes, which, however, could not be isolated. All the acids investigated, with the exception of acetic acid, yield hydrogen cyanide in large quantities.

According to Hantzsch, the formation of hydrogen cyanide by the action of nitric acid on organic substances is due to the intermediate

formation and decomposition of formaldoxime, according to the following scheme:



But since the oxime may also undergo decomposition by hydrolysis into hydroxylamine and formaldehyde, the latter substance may be expected as a product of all photochemical oxidations, resulting in the formation of hydrogen cyanide. This view is supported, not only by the experiments described above, but also by the simultaneous formation of hydrogen cyanide and formaldehyde by the action of nitric acid on ketones and ketonic acids containing the group  $R\cdot COMe$ . Acetone, methyl alkyl ketones, levulic and pyruvic acids, together with all substances (such as isopropyl alcohol, citric acid, and lactic acid) which may be oxidised to acetone, levulic acid, or pyruvic acid, yield both hydrogen cyanide and formaldehyde when oxidised by nitric acid.

The red colour observed during oxidations in the presence of ferric nitrate is considered by the author to be due to the formation of hydroxamic acids (compare Baudisch, this vol., ii, 523).

These results confirm the conclusion of Baudisch that the assimilation of nitrogen in plants is a photochemical process. F. B.

**Effect of Light on Insulation by Sulphur.** F. W. BATES (*La Radium*, 1911, 8, 312—313).—The mean leak of a leaf insulated by sulphur was found to be greater during the day than during the night. Strong sunlight much increased the leak, and this increase was reduced by interposing blue or red glass screens. In total darkness the leak during the day was reduced to practically the same value as at night. The increase is not due to increased ionisation of the air, nor to a photo-electric effect on the sulphur similar to that of ultra-violet light on zinc. The leak is the same whether the charge is positive or negative. By surrounding the sulphur, exposed to light, with a guard-ring, the leaf when charged oppositely to the guard-ring lost its charge and took an opposite charge. When the charges were similar in sign, they tended to become the same in magnitude in the light. In the dark the leaf lost its charge by ionisation of the air only, independently of the sign and amount of the charge on the guard-ring. The conductivity of the sulphur is thus increased by light. Ebonite shows a slight effect of the same kind, but amber is not influenced by light. F. S.

**The Number of Electrons Concerned in Metallic Conduction.** J. W. NICHOLSON (*Phil. Mag.*, 1911, [vi], 21, 245—266).—The view that the velocities of the effective electrons are distributed in accordance with Maxwell's law is shown to be in satisfactory agreement with Drude's experimental determinations of the optical constants of the metals. This assumption leads to values for the number of effective electrons in the atom, which are all very close to integers or half-integers, except in the case of cadmium. For nickel, cobalt, silver, copper, gold, magnesium, platinum, lead, tin, zinc, and aluminium the differences are all within the experimental limit of accuracy. The integers vary from two (nickel) to six (aluminium).

H. M. D.

**Ionic Mobility in Gases.** II. MAX REINGANUM (*Physical Zeitsch.*, 1911, 12, 666—671. Compare this vol., ii, 788).—Further arguments are advanced in support of the author's view that the observed high velocity, with which heavy ions move through gases of low density under the influence of an electric field, is in accordance with the requirements of theory. The calculated velocities of heavy ions are approximately equal to the velocity of the ions of the surrounding gas.

H. M. D.

**Certain Ionisation Effects Observed in Gases in Presence of Non-radioactive Substances.** Activity and Luminescence of Quinine Sulphate. MAURICE DE BROGLIE and L. BRIZARD (*Le Radium*, 1911, 8, 273—279. Compare this vol., ii, 174).—Experiments have been made to determine whether the scintillation exhibited by quinine and cinchonine sulphates when exposed to the air after being heated at 120° is connected with the ionisation of the surrounding gas.

It is found that those factors which increase the intensity or prolong the period of luminescence have a similar influence on the ionisation of the surrounding gas. The suggestion is made that both phenomena are connected with the triboluminescence of the crystals, and experiments are described in support of this view. In particular, the triboluminescent effect which is observed when crystals of either salt are rapidly cooled in liquid air is found to be accompanied by ionisation.

From observations of the action of luminescent quinine sulphate on photographic plates under different conditions, the authors draw the conclusion that the ionisation cannot be due to the emission of ultra-violet rays of the type which have been shown to have ionising properties. The photographic effects appear to be produced equally well through thin plates of glass and fluorite as through a thin layer of air. On the other hand, fluorite appears to prevent the ionisation of air on the further side of the plate. In explanation of the various facts, it is suggested that the conductivity of the gaseous medium in the vicinity of the luminescent crystals is due to minute electrical discharges which accompany the rupture of the crystals during the process of hydration (or dehydration). Those factors which would be expected to favour this discharge phenomenon are found by experiment to result in increased luminescence and increased ionisation.

H. M. D.

**The Ionisation of Liquid Hydrocarbons.** TCHESLAS BIALONJESKI (*Le Radium*, 1911, 8, 293—299. Compare Jaffé, Abstr., 1909, ii, 208; 1910, ii, 481).—The conducting properties of various fractions of American petroleum, when subjected to the influence of the  $\beta$ - and  $\gamma$ -rays of radium, have been investigated. The boiling points of the separate fractions, which were subjected to careful purification, were 47—52°, 52—58°, 58—70°, 75—82°, 82—90°, 90—105°, 150—200°, and 200—250°. The apparatus employed consisted of a condenser, the distance between the plates of which could be varied and accurately adjusted. Penetrating rays from

a radium preparation whose electrodes, to which the plates were immersed through the upper plate, which was in connexion with a Mullin electrometer, whilst the lower plate was connected with a battery, the potential of which could be varied from 4 to 864 volts.

Data are recorded which show the variation of the current with the applied potential difference for each hydrocarbon fraction with the condenser plates at a distance of 2 and 8 mm. For three fractions, experiments of the same kind were also made with a less active radium preparation. In a third series of measurements the three fractions 52—58°, 82—90°, and 200—250°, as well as vaselin, were investigated with the condenser plates at a distance of 0.5, 1, 2, and 4 mm.

From these data it appears that for small potential differences, the current diminishes rapidly as the boiling point of the hydrocarbon fraction rises, but that the current differences are relatively very much smaller when a strong electrical field is applied. At the highest potential differences the current approximates to a condition of saturation when the plates are close together, whereas at lower potentials the observed currents are not very different from those required by Ohm's law. With a less active radium preparation, evidence of saturation is obtained at smaller potential differences.

From the data of the last-mentioned series the author calculates the sum of the mobilities of the ions in cms. per second for a potential difference of one volt per cm.; these are respectively: fraction 52—58°,  $11.7 \times 10^{-4}$ ; 82—90°,  $3.7 \times 10^{-4}$ ; 200—250°,  $1.5 \times 10^{-4}$ ; vaselin,  $0.94 \times 10^{-7}$ . From these numbers it is evident that the mobility decreases very quickly as the boiling point rises, the decrease being more rapid than the increase in the viscosity.

As observed by Jaffé in the case of hexane, the current through the various hydrocarbon fractions exhibits a certain amount of unipolarity, and this is attributed to the presence of a certain proportion of ions of much smaller mobility than those which are mainly responsible for the conduction of the current. H. M. D.

**A New Radiant Emission from the Spark.** WALTER STEUBING (*Physikal. Zeitsch.*, 1911, 12, 626—630).—The rays emitted by a condenser spark passing between aluminium electrodes, which have been described by Wood (Abstr., 1910, ii, 915) as a new form of radiant emission, have been examined by the author, whose apparatus was closely similar to that employed by Wood. The experiments described indicate that the so-called new emission consists of rays from the spark discharge which have been scattered by the particles of metal in the vapour given off from the electrodes. These rays are independent of the nature of the gas in which the spark discharge takes place, and the emission is no longer observed if the spreading of the metal vapour is prevented by a rapid current of gas. If under these conditions a hermetically-sealed tube containing vapour of the metal is brought into the neighbourhood of the discharge, the emission effect is again observed. Resolution of the emission shows the absence of any bands, and the spectrum appears to be the same as that obtained directly from the spark discharge. H. M. D.

**Transformation of the Energy of Homogeneous Röntgen Radiation into Energy of Corpuscular Radiation.** CHARLES A. SADLER (*Phil. Mag.*, 1911, [vi], 21, 447—458).—The results obtained in a previous investigation (Abstr., 1910, ii, 251) have been further analysed. The author now arrives at the conclusion, that not only is there a very close connexion between the emission of corpuscular radiation and the production of homogeneous Röntgen radiation, but that there is strong evidence that, whenever the characteristic secondary radiation is excited, there is always produced a strictly proportional amount of corpuscular radiation. H. M. D.

**The Spectra of the Fluorescent Röntgen Radiations.** CHARLES G. BARKLA (*Phil. Mag.*, 1911, [vi], 21, 396—412. Compare Abstr., 1909, ii, 457; 1910, ii, 8).—A summary is given of the results which have been obtained in previous papers relative to the properties of the characteristic secondary or fluorescent rays which are emitted by metals under the influence of a primary X-ray beam. The fluorescent radiations which have been examined up to now fall into two distinct series, and it is probable that these include all fluorescent radiations which are actually emitted. Each element has its own characteristic fluorescent ray spectrum, which may be conveniently represented like an ordinary light spectrum, except that it is necessary to define the radiations by their absorption in some standard substance. The lines corresponding with the two series of rays move towards the penetrating end of the spectrum as the atomic weight of the emitting element increases. H. M. D.

**Dissymmetry of Positive and Negative Ions Relatively to the Condensation of Water Vapour.** E. BESSON (*Compt. rend.*, 1911, 153, 250—253).—Langevin's modification of C. T. R. Wilson's cloud chamber has been adapted to enable instantaneous microphotographs of the clouds produced to be obtained. An image of the positive crater of a powerful arc is formed in the chamber, and the cloud is viewed with a low-power microscope, the axis of which makes an angle of  $40^\circ$  with the pencil of illumination. Exposures of 0.02 second are employed, which are not sufficiently short to depict the droplets quite motionless.

The formation of the cloud has been observed in all its details. Alternate photographs, using X-ray ionisation, with the positive and negative ions respectively predominating, showed always a much larger cloud when the negative ions were in excess. F. S.

**The Mass of Gaseous Ions.** WILLIAM DÚANE (*Compt. rend.*, 1911, 153, 336—339).—To obtain evidence on the question of the existence of positive electrons, the ratios of the mass  $m$  to the charge  $e$  of the ions formed in air by the  $\alpha$ -rays of radium chloride was determined. The emanation from 0.3 gram of radium chloride was enclosed in a glass bulb of volume less than  $0.5 \text{ mm.}^3$ , with walls thin enough to allow the  $\alpha$ -rays to escape. This was placed outside the mica window of an apparatus, which could be exhausted to a very low vacuum, containing two metallic plates 2 cm. apart, one connected to

the electroscopes and the other to the battery. This was placed in a magnetic field, so that ions formed between the plates, under the combined action of the electric and magnetic fields, would pursue cyclonidal paths, and not reach the plates when these paths were sufficiently restricted. From the values of the electric and magnetic fields necessary to prevent the ions reaching the plates, the value of  $e/m$  could be calculated. The results were in accordance with the view that at low pressures the negative ions are entirely composed of electrons, and the positive ions of atoms or molecules of the gas.

No negative ions of molecular magnitude exist at low pressure, hence none are formed by loss of a positive electron from the molecule. The positive ions in air are all much larger than those in hydrogen, indicating that in air no positive ions of the order of magnitude of the hydrogen positive ion or less are formed. The conclusions are opposed to the hypothesis of the existence of positive electrons.

F. S.

**The  $\beta$ -Rays of the Radium Family.** J. DANYSZ (*Compt. rend.*, 1911, 153, 339—341).—The emanation, from 0.12 gram of radium chloride condensed in thin-walled Thuringian glass tubes, 5 mm. long, 0.3 mm. diameter, and 0.04 mm. thickness of wall, was used as the source. Becquerel's disposition was employed, whereby the trajectories of the several bundles of rays, coiled into circles by a magnetic field, were registered on a photographic plate. The results are ascribed to the small amount of matter in the neighbourhood of the source, and to the suppression of secondary rays which fog the plate uniformly. A magnetic spectrum of seven separate beams of rays, sharply separated from one another, was obtained. The approximate values of the velocities in terms of that of light, deduced by the Lorentz equation from the radii of curvature, are as follows:

Beam .....	I.	II.	III.	IV.	V.	VI.	VII.
Velocity .....	0.98	0.95	0.86	0.81	0.75	0.69	0.63

Exact determinations, and experiments to determine how the beams are distributed among the various members of the family are in progress.

F. S.

**Secondary  $\beta$ -Rays.** W. A. SCHAPOSCHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, *Phys. Part*, 187—195. Compare McClelland, *Abstr.*, 1908, ii, 650; Bragg and Madsen, *ibid.*, 921; Allen, *Phys. Rev.*, 1909, 29, 177; 1910, 30, 276).—The author's experiments show that, under the conditions employed, the penetrating power of the secondary rays does not depend on the magnitude of the angle of incidence, provided that the sum of the angles of incidence ( $\alpha$ ) and reflexion ( $\beta$ ) remains constant.

The mean values of the ratio  $J'/J$  for different angles of incidence, and under the condition  $\alpha + \beta = \text{constant}$ , are approximately equal to that corresponding with equality of  $\alpha$  and  $\beta$ , that is, with the condition of maximal secondary radiation.

With increase of the angle of incidence,  $\alpha + \beta$  remaining constant, the penetrating power of the secondary rays increases, that is, they become harder.

The composition of the secondary radiation, while the sum of  $\alpha$  and  $\beta$  is constant, does not change appreciably with change in the angle of incidence, and for the condition of maximum radiation,  $\alpha = \beta$ , it is the same as for non-equality of these two angles.

T. H. P.

**Some Chemical Effects of the Rays of Radium.** S. C. LIND (*Le Radium*, 1911, 8, 289—292).—The action of the rays of the emanation of radium and of the  $\beta$ - and  $\gamma$ -rays of radium on mixtures of hydrogen and bromine, and on hydrogen bromide gas, is too slow to be studied quantitatively. No measurable decomposition was observed in a tube filled to two-thirds of an atmosphere with hydrogen bromide after thirty-seven days' exposure to the penetrating rays of 0.2 gram of radium chloride. Neither is any combination of hydrogen and bromine detectable under the same conditions. The emanation of radium in equilibrium with 1 mg. of radium produced slight combination of the mixture (2.6% after fourteen days), but no decomposition of the compound. The rate of combination of the mixture in the dark at 303° was not appreciably increased by the presence of radium emanation. Anhydrous liquid hydrogen bromide is decomposed to a slight extent in the dark in presence of the emanation, about 3.5% of the energy of radiation being utilised in the decomposition in one experiment. Aqueous solutions of hydrogen bromide and potassium iodide are decomposed by the emanation in absence of light and of oxygen.

F. S.

**The Influence of Acids and Salts on the Amount of Radium Emanation Liberated from a Solution of Radium.** A. S. EYE and DOUGLAS MCINTOSH (*Trans. Roy. Soc. Canada*, 1910, [iii], 4, III, 67—68).—Various barium salts were found to contain from 2.84 to 0.11 ( $\times 10^{-12}$ ) gram of radium per gram, which must be taken account of in the measurement of minute amounts of radium. Sulphuric acid, barium chloride and sulphuric acid, and barium sulphate, respectively added to a standard solution of radium, reduced the emanation liberated on boiling 5, 87 and 73%. The amount of radium used was  $7.8 \times 10^{-10}$  gram.

F. S.

**$\delta$ -Rays.** NORMAN CAMPBELL (*Phil. Mag.*, 1911, [vi], 22, 276—302).—The velocity of the  $\delta$ -rays produced in plates and films of metals by the impact of  $\alpha$ -rays from polonium has been deduced from their behaviour in an electric field. The apparatus consisted of a metal plate connected with the electrometer placed opposite a slightly smaller hole in a metal box, the hole being covered with a thin metal foil capable of allowing  $\alpha$ -rays to pass through. Behind the foil inside the box was a plate coated with polonium. The value of the ionisation current was measured when the box was charged to different potentials, the plate connected to the electrometer being maintained at earth potential by a compensating current, by means of a potentiometer and high resistance. Certain negative conclusions have been drawn. There appears to be no difference between the speeds of the incident and emergent  $\delta$ -radiations. The speed of the  $\delta$ -rays appears to be independent of the speed of the  $\alpha$ -rays exciting them, and



probably as the materials from which the rays are emitted, although the possibility of reflection makes the interpretation of the results difficult. This, if correct, is of the utmost importance for the theory of ionisation, for the act of ionisation in gas is presumably similar to the expulsion of  $\beta$ -rays by solids. There is no evidence that the number of  $\beta$ -rays depends on the nature of the material, about ten being emitted for each  $\alpha$ -particle in the cases of the metals, copper, silver, gold, and aluminium, which were employed. Other conclusions are withdrawn in a subsequently-added note. In an appendix particulars are given of the high resistances employed. These are constructed of thermometer tube 13 cm. long, held in an earthed metal clamp, the electrodes being sealed into bulbs at the end, and are filled with a mixture of 1 part of alcohol to from 3 to 8 parts of xylene, dried by lime. They ranged from  $4 \times 10^{11}$  to  $7 \times 10^9$  ohms, and did not show any undesirable polarisation effects. F. S.

Concentration of the Radioactive Emanation of the Gases of Boracic Suffioni by means of Carbon at a Low Temperature. C. PORLEZZA and G. NORZI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 932—934).—The authors find that the radioactive emanation in the gas from the suffioni of Larderello can be concentrated by passing the gas over charcoal cooled to  $-77^\circ$  with solid carbon dioxide and ether. Under these conditions, all the emanation is absorbed, but only a portion of the other gases present, so that on heating the charcoal the gas evolved is thirty-four times more radioactive than was the gas treated. The gas employed for this concentration was previously freed from the carbon dioxide and hydrogen sulphide which it contains in large amount (94%).

R. V. S.

The Solubility of the Emanation of Radium in Organic Liquids. EVA RAMSTEDT (*Lq. Radium*, 1911, 8, 253—256).—The apparatus used consisted of a closed tube divided into two equal parts by a wide tap. One part was filled with the liquid under examination, and the other part with the emanation, usually two days' accumulation of 0.01 gram of radium chloride. Equilibrium was established

Liquids.	$18^\circ$ .	$0^\circ$ .	$-18^\circ$ .	da/a. dl.
Glycerol .....	0.21	—	—	—
Water .....	0.285	0.52	[0.39 at $9^\circ$ ]	0.031
Aniline .....	3.80	4.43	—	0.0190
Alcohol (abs.) .....	6.17	8.23	11.4	0.0163
Acetone .....	6.30	7.99	10.8	0.0168
Ethyl acetate .....	7.35	9.41	13.6	0.0174
Paraffin oil .....	9.2	12.6	—	—
Benzene .....	12.32	[16.34 at $3^\circ$ ]	—	—
Xylene .....	12.75	—	—	—
Toluene .....	13.24	18.4	27.0	0.0193
Chloroform .....	15.08	20.5	28.5	0.0182
Ether .....	15.08	20.9	29.1	0.0184
Hexane ( $66-70^\circ$ ) .....	16.56	23.4	35.2	0.0203
cycloHexane ( $80^\circ$ ) .....	18.04	—	—	—
Carbon disulphide .....	23.14	33.4	50.3	0.0210

by allowing the liquid to flow from one part of the tube to the other several times. The tap was closed and the tube left five hours, and the  $\gamma$ -radiation of the two parts successively measured in a suitable condenser. The table on p. 842 gives the result.  $a$  denotes the coefficient of solubility at the temperatures given, and  $da/adt$  the proportionate increase of the coefficient by  $1^\circ$  lowering of temperature from zero. The results fully bear out those of other investigators: all organic liquids examined, except glycerol, absorbing more than water, carbon disulphide absorbing six times more than aniline and eighty times more than water. The volatile and very mobile liquids appear to absorb more than the non-volatile and viscous, but there are exceptions. F. S.

**Action of the Radium Emanation on Thorium Salts.**  
HEINRICH HERSCHFINKEL (*Compt. rend.*, 1911, 153, 255—257).—The experiments of Ramsay and Usher (*Trans.*, 1909, 624; *Abstr.*, 1909, i, 850) have been repeated to see if the formation of carbon dioxide from thorium salts under the action of radium emanation was not due to organic impurities in the salt. The thorium nitrate employed was specially purified by Merck to avoid as far as possible these impurities. The emanation in equilibrium with 0.1 gram of radium acting on 125 grams of the thorium nitrate for twelve days, produced 1 c.c. of carbon dioxide. The solution left without emanation for the same time, or the emanation acting on distilled water, gave only traces of carbon dioxide. Small quantities of potassium permanganate gave more carbon dioxide than the emanation. The impurity present is probably a trace of oxalic acid. The formation of carbon dioxide by the action of the emanation does not prove the transformation of the thorium atom into carbon. F. S.

**Action of Niton (Radium Emanation) on Thorium Salts.**  
SIR WILLIAM RAMSAY (*Compt. rend.*, 1911, 153, 373—374).—Herschfinkel's experiment (preceding abstract) only proves that his specimen of thorium contains compounds capable of yielding carbon dioxide by the action of permanganate. In the author's first experiments the thorium nitrate was not exposed to radium emanation, but yielded quantities of carbon dioxide proportional to the time of accumulation. To settle the question whether the carbon was derived from the transformation of the thorium, a specimen of thorium nitrate was prepared by heating to redness, and solution of the product in nitric acid. The solution was crystallised many times with precautions to exclude dust, and some c.c. of solution from well formed crystals of the salt were exposed to the radium emanation from 0.6 gram of radium bromide, purified by long contact with moist potassium hydroxide, which had not come into contact with grease or rubber. Carbon dioxide was always found in the gas. Nitrates of bismuth, mercury, and silver gave no trace of carbon dioxide. F. S.

**Molecular Weight of the Thorium Emanation.** MAY SYBIL LESLIE (*Compt. rend.*, 1911, 153, 328—330).—Using Debiere's

apparatus (Abst. 1910, ii, 675) with some modifications, the molecular weight of the thorium emanation has been determined by the method of effusion through a small hole in a plate. A preparation of radio-thorium is the source of emanation which diffuses into a vessel containing a cylinder, the activity imparted to which furnishes a measure of the emanation present. The activity is measured with the vessel closed and open through fine holes in a platinum plate to a large, exhausted receptacle, the time of exposure varying from one to four days. The experiments are done at a pressure of a few hundredths of a millimetre of mercury. If  $q$  and  $q'$  are the activities with the vessel open and closed,  $\mu$  and  $\lambda$  the coefficients respectively of effusion and decay of the emanation,  $q/q' = \lambda + \mu/\lambda$ . The coefficient of effusion of oxygen is determined in the same apparatus, and the molecular weight of the emanation obtained from the inverse ratio of the squares of the coefficients of effusion. According as 54 and 53.3 seconds are accepted for the half-period of the thorium emanation, the molecular weight in the one day's experiments is 210 or 203, and in the two days' experiments either 201 or 194. An error of 1% in the activity measurements makes a 5% error in the calculated molecular weight, but the experiments show clearly that the molecular weight is in the neighbourhood of 200.

F. S.

The Disintegration Products of Uranium. GEORGE N. ANTONOFF (*Phil. Mag.*, 1911, [vi], 22, 419-432).—Uranium nitrate, specially purified from other radio-elements by adding lanthanum or thorium and precipitating these with oxalic acid, and in other ways, was employed. The uranium- $X$  was separated in two ways, the first by precipitating barium sulphate in the solution, and the second by adding an iron salt and precipitating it by boiling. The first product showed a normal decay curve, both when measured bare and when covered with sufficient aluminium foil to absorb the soft  $\beta$ -rays. The second product showed a normal decay curve under the latter conditions, but a larger proportion of soft  $\beta$ -rays were initially present which decayed with a half-period of 1.5 days. This is attributed to a new product, termed uranium- $Y$ , which could only be separated in very small amount from the uranium, and which gave a very feeble  $\alpha$ -radiation as well as the soft  $\beta$ -radiation. The latter has a coefficient of absorption,  $\mu(\text{cm.})^{-1}$ , about 300, and causes about 25% of the total ionisation. The latter was only about 1/60,000th of that given by the uranium from which it was separated. It cannot be the second  $\alpha$ -ray product of uranium on account of the large proportion of  $\beta$ -radiation. Thin layers of uranium oxide do not show any  $\beta$ -radiation other than that of uranium- $X$ . The  $\beta$ -ray recovery curve of uranium shows no evidence of the regeneration of uranium- $Y$ . In absence of any definite evidence as to the connexion of uranium- $Y$  with uranium, it is suggested that it may be a branch product of uranium. In chemical nature the product resembles uranium- $X$ , and has not been separated from it.

F. S.

Attempts to Prepare Metallic Radium. HEINRICH HERSCHE-  
FINKEL (*J. Radiochem.*, 1911, 8, 299-301).—The attempt to prepare

metallic radium by decomposing the azoimide by heating in a vacuum (Ebber, *Abstr.*, 1910, ii, 1024) is not in agreement with the facts found by Mme. Curie and Debierne that radium is not volatile at  $100^{\circ}$  in a vacuum, and very readily forms nitride in presence of nitrogen. Repetitions of the experiment gave no metallic sublimate, but a dark product and nitrogen. The product probably contains a very little alkaline-earth metal, very impure, and contains nitride. Pure barium azoimide, on rapid heating to explosion in a vacuum, gives only 86% of its nitrogen as gas. On rapid heating to  $600^{\circ}$  in a vacuum, it melts and gives yellow drops, which have an odour of acetylene, and become white in the air. Curtius's method of preparing the alkaline-earth metals thus gives very impure products. F. S.

**The Properties of Technically Prepared Mesothorium and its Evaluation.** OTTO HAHN (*Chem. Zeit.*, 1911, 35, 845—846).—

An account is given of the well-known chemical and radio-active properties of mesothorium (compare this vol., ii, 8; *Trans.*, 1911, 99, 72). The monazite sand from which mesothorium is technically prepared contains 0.3% U and 4—5%  $\text{ThO}_2$ , and the activity is due, 75% to mesothorium and 25% to radium. In this mesothorium the maximum activity is reached in 3.2 years, whilst after ten years the activity is still somewhat greater than when prepared, and after twenty years is about half as great. When purified from inactive material the activity is four times greater than that of pure radium compounds, the weight of mesothorium present being estimated at 1%, the remainder being radium. The strength of the activity is compared with that of pure radium compounds by means of an air-tight electroscope of brass, of wall thickness 1—2 mm., lead plates being interposed if necessary, of thickness not greater than 0.5 cm. Under these conditions the  $\gamma$ -rays are compared, the somewhat greater absorptibility of the  $\gamma$ -rays of mesothorium not affecting the measurements more than a few per cent. F. S.

**The Ratio between Uranium and Radium in the Active Minerals.** Mlle. ELLEN GLEDITSCH (*Le Radium*, 1911, 8, 256—273).

Compare *Abstr.*, 1909, ii, 533, 714).—A full description is given of the methods employed in determining radium and uranium, and the subject is discussed from the point of view of all the publications made since the first results of the author were published. Results are given for twenty-one specimens of minerals, including chalcocite, carnotite, gummite, autunite, pitchblende, samarskite, broeggerite, uranophane, fergusonite, and thorianite. The proportion of radium to uranium varies from 1.82 to  $3.74 \times 10^{-7}$ . The minerals with highest ratio come from Cornwall (one chalcocite and one pitchblende), next comes a Ceylon thorianite (the only one included), next six minerals from Norway. The variations in the ratio are considered to be established, and are ascribed possibly to the existence of intermediate substances between uranium and radium with period comparable with that of uranium itself, or to the influence of the external conditions or of the presence of other active elements on the rate of transformation. F. S.

The Radioactive Tufa of Fiumi. Occluded Gases Content of Radium and Uranium. C. BONAZZI and G. NOZZI (*Atti R. Acad. Lincei*, 1911, [v], 29, 1, 935-939. Compare NASINI and LEVI, Abstr., 1908, ii, 401).—The tufa of Fiumi contains occluded helium only in very small quantities. The quantity of radium present in a gram of the rock is high, amounting to  $5 \times 10^{-12}$  gram. The quantity of uranium is  $0.76 \times 10^{-5}$  gram per gram of rock.

R. V. S.

Radioactivity of the Gas Obtained from the Thermal Springs of S. Saturnino (Benetutti-Sardegna). ARMANDO BERNINI (*Nuovo Cim.*, 1911, [vi], 1, i, 455-461).—The conductivity of the gaseous mixture increased for about three hours, attaining a maximum value nearly twice the initial activity. The same phenomenon has previously been observed by Rutherford and Soddy for radium emanation. The rate of decay of the induced radioactivity and other data prove that the activity of the mixture in this case is due to radium emanation. The slight radioactivity of the water which has also been measured is due to the presence of a little of the radioactive gas in solution.

G. S.

The Amount of Radium and Radium Emanation Present in the Water and Gases of the Caledonia Springs, near Ottawa. A. S. EVE (*Trans. Roy. Soc. Canada*, 1910, [iii], 4, III, 53-54).—The amount of radium in the spring water varies from 10 to  $18 \times 10^{-12}$  gram of radium per litre, whilst the amount of radium emanation corresponds with between 620 and  $210 \times 10^{-12}$  gram of radium per litre of gas, which is from 4000 to 6000 times the amount present in the atmosphere. The water from Quelle am Schweizergang, Joachimsthal, the most radioactive known, is about 7000 times as active as that of the Caledonia Springs.

F. S.

The Radium Contents of Specimens from a Deep Boring at Beachville, Ontario. A. S. EVE and DOUGLAS MCINTOSH (*Trans. Roy. Soc. Canada*, 1910, [iii], 4, III, 69-70).—A determination of the amount of radium in samples varying from a depth of 30 feet to 2580 feet showed a fairly uniform distribution of radium, between  $0.5$  and  $1.42 \times 10^{-12}$  gram of radium per gram, the mean being 1.02, which is in agreement with the values found for other materials of the earth's crust. The solution obtained by leaching with water the material, after fusion with alkali carbonate, contained on the average one-fourth of the total radium. There was no relation between the depth and the amount of radium.

F. S.

The Probable Influence of the Soil on Local Atmospheric Radioactivity. JAMES COX SANDERSON (*Amer. J. Sci.*, 1911, [iv], 32, 169-184).—A current of air from a tube buried about 120 cm. beneath the floor of the Physical Laboratory, New Haven, U.S.A., was drawn through the ionisation chamber of an electroscope. The natural leak of the instrument immediately increased eighteen times.

and continued to increase at first rapidly, then more slowly for three hours, and then very gradually for three days, when it attained a maximum. This is what is to be expected if both radium and thorium emanations are present in underground air. By variations of the experiment the proportion of the effect due to the thorium and radium emanations separately was found. The effect due to the thorium was standardised in terms of a known weight of thorium by passing air into the electroscope through sand to which a known quantity of thorite in solution had been added. The amounts of thorium in various soils and other materials were estimated by comparison with the standard. Since the emanating power of the standard is probably a maximum and greater than that of the materials tested, the quantities of thorium so found are necessarily a minimum; thus solid monazite and thorianite crystals possessed respectively 420 and 6100 times less emanating power per unit of thorium than the standard. The results were that 1 c.c. of underground air contained radium emanation in equilibrium with  $2.4 \times 10^{-13}$  gram of radium, and that 1 c.c. of the earth emits thorium emanation equivalent to that produced by  $1.35 \times 10^{-6}$  gram of thorium. The radium value is 4000 times that found by Eve for the atmosphere at Montreal, and the thorium value is one-tenth of that found by Joly for the average of many common rocks.

F. S.

**Electrical Conductivity of Salts and Mixtures of Salts.** ALFRED BENRATH and J. WAINOFF (*Zeitsch. physikal. Chem.*, 1911, 77, 257—268).—The measurements were carried out as described in a previous paper (compare Abstr., 1909, ii, 12). The electrical conductivities of the binary systems  $\text{AgCl-KCl}$ ,  $\text{KCl-NaCl}$ , and  $\text{KCl-K}_2\text{CrO}_4$ , and of the components were determined at a series of temperatures up to the melting points of the individual salts.

The conductivities of the single salts are represented fairly satisfactorily by the formula  $\log K = a + bt$ , where  $K$  is the specific conductivity at the temperature  $t$ , and  $a$  and  $b$  are constants. As regards the binary systems, silver and potassium chlorides are not miscible in the solid state, and the conductivity of the system is the sum of the conductivities of the components. The chlorides of potassium and sodium are miscible in the solid state in all proportions, and the conductivity of the mixtures is greater than that of the components, the isothermals rising fairly rapidly from the points representing the conductivities of the salts. Potassium chloride and potassium chromate are not miscible in the solid state, except for mixtures containing 0—4% of the former salt. The curve obtained by plotting the conductivities as ordinates against the composition of the mixture as abscissae shows a distinct maximum with no definite breaks. The form of conductivity curve to be anticipated for such systems is discussed.

At the melting points and other transition points there are sudden, and sometimes very great, alterations in the resistance. At the transition point the conductivity of the red modification of potassium chromate is six times that of the yellow form.

G. S.

**Mercurous Sulphate as Depolariser in Normal Elements.** GEORGE A. HUNTER (*Zeitsch. physikal. Chem.*, 1911, 77, 411-419. Compare Abstr., 1904, ii, 695; *Phys. Rev.*, 30, 648; van Ginneken, this vol., ii, 179).—A theoretical paper in which van Ginneken's views on this subject are adversely criticised. The assumption that the mercury ion concentration diminishes steadily with the progress of hydrolysis appears to be opposed to the experimental data. The author upholds his earlier views on the subject. G. S.

**Rapid Formation of Lead Accumulators with Solutions of Sulphuric Acid and Chlorate or Perchlorate.** G. SCHLEICHER (*Zeitsch. Elektrochem.*, 1911, 17, 554-569).—The rapid production of lead plates carrying an adherent coating of lead peroxide suitable for use in an accumulator by alternate electrolytic oxidation and reduction of the lead in solutions of sulphuric acid containing varying quantities of a chlorate or perchlorate is studied. The results are almost identical with those obtained by Just, Askenasy, and Mitrofanoff (Abstr., 1910, ii, 96), using an addition of nitric acid in place of the chlorate or perchlorate. The perchlorate is preferable to the other substances, because it is not reduced at the cathode. T. E.

**The Electromotive Behaviour of Ternary Alloys. The Ternary System Zinc-Silver-Lead.** ROBERT KREMANN and F. HOFMEIER (*Monatsh.*, 1911, 32, 597-608).—Measurements of the *E.M.F.* of the cell  $\text{Zn} | \text{N}/1\text{-ZnSO}_4 | \text{Ag-Zn alloy}$  give results in good agreement with those of Herschkowitch (Abstr., 1898, ii, 583). Similar measurements with ternary alloys of zinc, lead, and silver show that when the ratio  $\text{Ag} : \text{Zn}$  is from 0:100 to 30:70, the potential is entirely unaffected by the presence of lead. The alloy in which the ratio is 30:70 has the same potential as lead, and alloys richer in silver generally give the potential of lead, except in accidental cases, when the particles of lead do not come into contact with the solution. The potential when obtained is that of the corresponding silver-zinc alloy. The results show that lead does not form solid solutions with zinc and silver. C. H. D.

**Equilibria and Potentials at Membranes in the Presence of Non-dialysing Electrolytes.** FREDERICK G. DONNAN (*Zeitsch. Elektrochem.*, 1911, 17, 572-581).—Two solutions, 1 and 2, separated by a membrane are considered. Solution 1 contains a salt,  $\text{NaR}$ , the anion of which cannot pass through the membrane; solution 2 contains a salt, for example, sodium chloride, both the anion and cation of which can pass through it. When equilibrium is reached the cations and anions will be divided between the two solutions in such a way that the reversible, isothermal transference of one mol. of  $\text{Na}^+$  and one mol. of  $\text{Cl}^-$  from one solution to the other can be effected without expenditure of work. From this it follows that  $[\text{Na}^+]_1[\text{Cl}^-]_1 = [\text{Na}^+]_2[\text{Cl}^-]_2$ , where the bracketed symbols represent equilibrium concentrations. Assuming complete dissociation of both electrolytes and equal volumes of the two solutions, it follows that  $x = c_1^2/(c_1 + 2c_2)$ , where  $c_1$  and  $c_2$  are the initial concentrations of  $\text{NaR}$  and  $\text{NaCl}$  in solutions 1

and 2 respectively, and  $x$  is the diminution of concentration of the sodium chloride by diffusion from 2 to 1. From this it is easily seen that the presence of the salt NaR in sufficient relative concentration on one side of the diaphragm has the effect of making the diaphragm almost impermeable for sodium chloride in the direction 2 to 1, whilst it remains freely permeable in the reverse direction.

The case of two electrolytes with no common ion (NaR and KCl, for example) is then treated in exactly the same way. Calling  $x$  the diminution of concentration of the K<sup>+</sup> ions, and  $y$  that of the Cl<sup>-</sup> ions in solution 2,  $x = (c_1 + c_2)c_2/(c_1 + 2c_2)$  and  $y = c_2^2/(c_1 + 2c_2)$ . The effect of a relatively large concentration of the salt NaR is that the greater part of the potassium ions in solution 2 diffuses through the membrane into solution 1, whilst the chlorine ions remain behind in solution 2.

When a solution of non-dialysing electrolyte NaR is separated by the diaphragm from pure water or a very dilute solution of an alkali, it is shown that sodium ions will pass from 1 to 2, which is only possible if they are accompanied by an equal number of hydroxyl ions formed by dissociation of the water. The solution remaining in 1 is therefore acid and the salt NaR partly decomposed. If the acid HR is weak, this membrane hydrolysis may become very large.

Owing to the differences in the concentrations of the ions in the two solutions separated by the membrane, there is a difference of electrical potential between them. By means of a reversible, isothermal cycle of operations, it is shown that the difference of potential  $\pi_1 - \pi_2 = RT/F \log \lambda$ , where  $\lambda = [\text{Na}^+]_2/[\text{Na}^+]_1 = [\text{Cl}^-]_1/[\text{Cl}^-]_2 = [\text{OH}^-]_1/[\text{OH}^-]_2$ .

The many important applications which the theory may have in physiology are pointed out. T. E.

**Electrolysis of Solutions of Salts of Fatty Acids in the Corresponding Anhydrous Acids.** KARL HOPFGARTNER (*Monatsh.*, 1911, 32, 523—561).—The electrolytic decomposition of alkali acetate dissolved in glacial acetic acid, of alkali propionate in anhydrous propionic acid, and of sodium formate in formic acid has been investigated, and the influence established of concentration, temperature, and current density on the gases liberated.

Qualitatively the products of electrolysis in the anhydrous acid solutions are the same as those given by acidified aqueous solutions of the same salts, but quantitatively the proportions are very different. An exception is afforded by the formation of carbon monoxide from formate, and possibly of butylene from propionate.

The effect of an increase of temperature, of concentration, or of current intensity is also in the same sense as in aqueous solutions, but quantitatively it is much less in the case of the anhydrous acid solutions.

Accordingly in both cases the main reactions must be the same, and any formulation of the changes which take place must exclude all reactions in which water plays a part. E. F. A.

**Formation of Hydrogen Cyanide in the Electric High Tension Arc.** A. V. LIPINSKI (*Zeitsch. Elektrochem.*, 1911, 17, 761—764).—Mixtures of methane, nitrogen, and hydrogen, the composi-



tion of which varies between the limits  $\text{CH}_4$  82%,  $\text{N}_2$  16%,  $\text{H}_2$  16%, and  $\text{OH}$ , 34%  $\text{N}_2$ , 53%,  $\text{H}_2$  15% are used. An alternating current are at 2000 volts and 0.05 to 0.12 amperes is passed through 3.8 litres of the mixture for one to three hours between platinum terminals. The hydrogen cyanide formed is then estimated. Carbon is deposited from mixtures containing more than 20% of methane. With this mixture the whole of the methane can be converted into hydrogen cyanide (compare this vol., ii, 790). T. E.

Use of the Magnetic Field in Determining Constitution. X. PAUL PASCAL (*Bull. Soc. chim.*, 1911, [iv], 9, 809-812. Compare this vol., ii, 464).—Although the rules already enumerated in previous papers of this series for the calculation of molecular magnetic susceptibilities give results in close agreement with those determined experimentally, there are a certain number of apparent exceptions in the case of tautomeric compounds, some of which have been dealt with already (Abstr., 1909, ii, 869). *cycloHexanone* has a mol. susceptibility  $-661 \times 10^{-7}$ ; the *keto*-form should have the value  $-631 \times 10^{-7}$ , and the *enol*-form the value  $-669 \times 10^{-7}$ , whence it appears that the equilibrium mixture at atmospheric temperature contains 78% of the latter form (compare Harding, Haworth, and Perkin, *Trans.*, 1908, 93, 1943). In the *methylcyclohexanones* the equilibrium moves towards the *keto*-form as the methyl group approaches the carbonyl group; thus the *meta*-isomeride contains 53% *enol* form, and the *ortho*-isomeride only 35%.

Resorcinol and phloroglucinol, examined in a solid state, behave as pure phenols in the magnetic field, and quinone as a diketone, whilst nitrosophenol and dinitrosoresorcinol behave as quinonoximes. The molecular susceptibilities of a number of compounds of these types are given, with the percentages of *enol*-form in the equilibrium mixture at the ordinary temperature. T. A. H.

Solutions of Salts Heterogeneously Magnetic in a Heterogeneous Magnetic Field. C. STĂNESCU (*Compt. rend.*, 1911, 153, 547-549).—A solution of a paramagnetic substance in a glass cell was rendered heterogeneous by adding water, so that the solution and water were separated by a zone of varying concentration. The cell being illuminated and placed between the poles of an electromagnet, was viewed through a slit placed at the focus of a double convex lens. On establishing the magnetic field, layers of different concentrations were seen to arrange themselves in a series of concentric equipotential surfaces, the most concentrated round the poles. The phenomenon is shown very indistinctly by diamagnetic salts, owing to the small magnetic permeability of these substances. W. O. W.

Conception of the Pressure of Expansion. L. GAR  
(*Compt. rend.*, 1911, 153, 262-264. Compare Abstr., 1910, ii, 1043).—A mathematical paper relating to the pressure exerted by one constituent of a binary mixture if it remained in the ideal state of a perfect gas and in equilibrium with the fluid solvent. The results (Abstr., 1910, ii, 184) for solutions of carbon dioxide are confirmed. W. O. W.

**Relationships between Atomic Heat, Coefficient of Expansion, and Compressibility of Solid Elements.** EDUARD GÄRTNER (Ber. deut. physikal. Ges., 1911, 13, 491—503. Compare Abstr., 1910, ii, 824).—In connection with the theory of solid monatomic elements, it is shown that the thermal expansion and the change of compressibility with temperature at low temperatures can be expressed in terms of the characteristic atomic frequency and its variation with volume or pressure. Data for copper, platinum, and iron are utilised in showing the relationships which are involved.

H. M. D.

**Modulus of Elasticity and Thermal Expansion of Metals.** H. SIEGLERSCHMIDT (Ann. Physik, 1911, [iv], 35, 775—782).—It is shown that the relationship between the elastic and thermal properties of a large number of metals can be expressed by means of the equation  $E/s = C(1/\beta)^n$ , in which  $E$  is the elastic modulus,  $s$  the density,  $A$  the atomic weight,  $\beta$  the coefficient of thermal expansion, and  $C$  and  $n$  are constants.

H. M. D.

**Thermo-calorimetric Measurements.** R. MELLECEUR (Ann. Chim. Phys., 1911, [viii], 23, 556—566).—A form of calorimeter, indicated by Regnault (Compt. rend., 1870, 70, 664), has been tried in the measurement of the specific heat of liquids. The liquid is contained in a cylindrical reservoir, surrounded by an annular space containing mercury, which serves as thermometric substance. This piece of apparatus is suspended centrally in a chamber with blackened walls, the chamber being immersed in a bath of constant temperature. The temperatures of the liquid under examination and of the outside bath having been suitably adjusted, observations of the rate of cooling of the liquid are taken.

From experiments with water, benzene, acetone, acetic acid, and carbon disulphide, it is found that results accurate to about 1% can be obtained with this apparatus when certain precautions are taken. Exhaustion of the chamber in which the cooling liquid is suspended makes the rate of cooling too small for the purpose of ordinary laboratory measurements.

H. M. D.

**Calculation of Specific Heats of Simple Solutions.** N. P. PASCHKY (J. Russ. Phys. Chem. Soc., 1911, 43, Phys. Part, 166—184).—The author first discusses the various formulæ which have been given for the calculation of specific heats of solutions, and then deduces formulæ in the following manner.

If  $\delta$  and  $s$  represent respectively the specific heat and density of a solution containing  $X$  grams of solvent and  $Y$  grams of solute per c.c., and  $\Phi$  and  $\theta$  are the specific heats of the solvent and solute respectively, the law of mixtures would give:

$$\delta s = X\Phi + Y\theta \dots \dots \dots (1);$$

allowing for possible variations of  $\Phi$  and  $\theta$  with concentration, this equation takes the form (2)  $\delta s = X(\Phi - \Delta_1) + Y(\theta + \Delta_2)$ .

A necessary condition for the validity of this expression is

$$X\Delta_1 - Y\Delta_2 = 0 \text{ or } \Delta_1/\Delta_2 = Y/X.$$

In order to allow for possible divergence from this normal case,

the ratio  $\Delta_1/\Delta_2$  may be equated to  $\alpha Y/bX$  (3), where  $\alpha$  and  $b$  are constants and  $\alpha$  may be greater than, equal to [as in equation (2)], or less than, 1. Equation (3) may be satisfied in two ways:

$$[A] \Delta_1 = \alpha Y \Delta_2 \text{ and } \Delta_1 = b X \Delta_2,$$

where  $\Delta_2$  is a constant, or

$$[B] \Delta_1 = \alpha \Delta_2' / X \text{ and } \Delta_2 = b \Delta_2' / Y.$$

Of these, [B] leads to no new expression, but application of [A] to equation (2) gives:

$$\delta s = X\Phi + Y\theta + (b - \alpha)XY\Delta_2, \quad (4),$$

which is the general form for the calculation of specific heats of solutions of non-electrolytes.

Similarly, for electrolytes,  $\Delta_1/\Delta_2 = \alpha i Y/bX$ , where  $i = [1 + (n-1)\alpha]$ ,  $n$  being the number of active particles which can be formed by a molecule of the electrolyte and  $\alpha$  the degree of dissociation. Substitution of  $\Delta_1 = \alpha i Y \Delta_2$  and  $\Delta_2 = b X \Delta_2$  in equation (2) gives:

$$\delta s = X\Phi + Y\theta - \alpha(n-1)\alpha XY\Delta_2 + (b - \alpha)XY\Delta_2,$$

which is the general form for the calculation of the specific heats of electrolytic and all other simple solutions. For solutions of normal electrolytes alone, this expression becomes:

$$\delta s = X\Phi + Y\theta - \alpha(n-1)\alpha XY\Delta_2.$$

Application of these expressions to solutions of a number of salts and organic compounds indicates their validity. In general, it is found that the specific heat of a substance changes when it is dissolved.

The method employed for the experimental determination of specific heats of solutions is described. T. H. P.

**Latent Heat of Fusion and Specific Heat of Fatty Acids.** GUSTAVE MASSOL and A. FAUCON (*Compt. rend.*, 1911, 153, 268-270. Compare Abstr., 1909, ii, 791).—Formic and acetic acids have given results analogous to those already described for propionic acid. Lauric acid was found to have a latent heat of fusion 46.68 Cal., whilst the latent heat of solidification was 37.42 Cal. The difference was greater for slightly impure acids, and is attributed to the presence of two modifications, a crystalline form having discontinuous physical properties at the melting point, and an amorphous form showing continuous variation in properties in the interval between complete solidification and liquefaction. W. O. W.

**Comparison of Platinum Thermometers with the Nitrogen, Hydrogen, and Helium-Thermometer, and the Determination of Certain Fixed Points between 200° and 450°.** LUDWIG HOLBORN and F. HENNING (*Ann. Physik*, 1911, [iv], 35, 761-774).—From a comparison of the records of platinum-resistance thermometers with those of various gas thermometers, three of which contained nitrogen, hydrogen, and helium respectively in bulbs of Jena glass 59<sup>11</sup>, and the fourth, nitrogen in a quartz bulb, the authors find that the temperatures recorded by the resistance thermometers between 200° and 450° are probably correct within 0.1°. For this interval, C. V. Hendar's formula holds quite satisfactorily.

In connexion with this thermometric comparison, the following fixed points were determined: freezing points—tin, 231.83°; cadmium,

320.92°; zinc, 419.40°; boiling points—naphthalene, 217.96°; benzophenone, 306.69°; sulphur, 444.51°. The boiling-point values in particular are in good agreement with those recorded by Callendar and Griffiths and by Waidner and Burgess.

H. M. D.

**Experiments with Liquid Helium-*E*. A Helium Cryostat.** H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 204-210. Compare this vol., ii, 368, 487, 575, 687).—A modified form of helium cryostat is described, in which the cryostat chamber is separated from the helium liquefier by a valve, and in which the liquid helium is syphoned over from the liquefier through a well-cooled syphon tube.

H. M. D.

**Thermoelectric Method of Cryoscopy.** HENRY H. DIXON (*Proc. Roy. Dublin Soc.*, 1911, 13, 49-62).—A differential method of determining small differences in the freezing points of solutions is described in detail. Two test-tubes, one containing water, the other the solution the freezing point of which is to be determined, are placed side by side in a larger test-tube acting as air chamber; the large tube is immersed in a freezing mixture. As thermoelement, copper-eureka junctions proved suitable; they were connected with a galvanometer in the usual way, as few contacts as possible being used. Corrections were applied for the difference between the temperature of the freezing mixture and that of the solution at its freezing point. The chief source of error in the experiments is the occurrence of thermo-*E.M.F.*'s, owing to differences of temperature at the metallic junctions, and to eliminate these as far as possible the galvanometer had to be placed in a thermostat. When the water and the solution have been cooled just below their freezing points, separation of ice is started by adding a minute amount of ice, and the solutions are stirred continuously while readings are being taken.

G. S.

**Cryoscopy of Certain Mineral Acids and Phenols.** EUGÈNE CORNU (*Compt. rend.*, 1911, 153, 341-343. Compare Abstr., 1909, ii, 972; 1910, ii, 121).—The author continues his studies of the curves representing the variations of the lowering of freezing point of acids undergoing progressive neutralisation by alkali hydroxides.

The graphs for chloric acid, perchloric acid, and phenol correspond with that of a monobasic acid. That of iodic acid shows a minimum corresponding with the normal salt, but is remarkably rectilinear up to this point, giving no indication of the existence of an acid having the double formula. Selenious, dithionic, and carbonic acids and resorcinol behave as dibasic acids; pyrophosphoric acid as tetrabasic. This method may be applied to acids too weak to influence the ordinary indicators, but not to such feeble acids as hydrogen sulphide.

Boric acid on neutralisation with potassium hydroxide behaves as if some molecules of the acid united with molecules of the monopotassium salt, forming condensed salts. It appears to be monobasic, and to contain only one boron atom in the molecule. Arsenious acid behaves in the same way.

A new type of curve has been found in the case of chronic acid and periodic acid, due to phenomena other than those of simple neutralisation.

W. O. W.

**Solidification Points of Some Organic Liquids.** JEAN TIMMERMAN (*Bull. Soc. chim. Belg.*, 1911, 25, 300-326).—In the first part of the paper the author discusses the various kinds of thermometers for use in low temperature work. He makes use of a platinum resistance thermometer for standardising his thermometers filled with different liquids (compare Abstr., 1909, ii, 121). Toluene and amylene are recommended as the best liquids with which to fill thermometers for such work, provided that they are not subjected to too rapid variations in temperature.

In the second part of the paper the results are given, to  $0.1^\circ$  of the determinations of the solidification points of some sixty pure organic liquids. From his results with ether the author draws the conclusion that solid ether is dimorphous, the stable form solidifying at  $-116.2^\circ$  and the unstable form at  $-123.3^\circ$ , the latter only being obtainable by slow cooling.

W. G.

**Isotherms of Monatomic Substances and of their Binary Mixtures. XI. The Critical Temperature of Neon and the Melting Point of Oxygen.** H. KAMERLINGH ONNES and C. A. CROMMELIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 163-165). Compare this vol., ii, 203, 467).—A vacuum jacketed cryostat, containing liquid oxygen and surrounded by a similar larger vacuum tube containing liquid air, was connected with a vacuum pump of large capacity and the pressure on the oxygen reduced. At a pressure of 1 mm., solid oxygen began to separate out, and the freezing point thus obtained was  $-218.4^\circ$ . This differs considerably from the values given by Rankine ( $-210.4^\circ$  and  $-212.0^\circ$ ), and by Estreicher ( $-227^\circ$ ).

When a piezometer tube containing neon was introduced into the liquid oxygen cryostat at  $-218.4^\circ$ , the raising of the pressure to sixty atmospheres did not produce any trace of liquid neon. This indicates that the critical temperature of neon is below  $-218^\circ$ .

H. M. D.

**Densities of Co-existing Phases (Orthobaric Densities) and the Diameter for Sulphur Dioxide in the Neighbourhood of the Critical Point.** ETTORE CARDOSO (*Compt. rend.*, 1911, 153, 257-259).—Determinations of the rectilinear diameter were made, using Natterer tubes in pairs. The influence of stirring and of temperature was studied, and the results will be published later. When the liquid phase only was stirred, the diameter was found to be perfectly rectilinear to within  $4^\circ$  of the critical point, when a distinct inflection appeared. Extrapolation of the rectilinear diameter gave  $0.520$  as the critical density.

W. O. W.

**General Relationship between Heat of Vaporisation, Vapour Pressure, and Temperature.** IVAR W. ANDERBERG (*Zeitsch. physikal. Chem.*, 1911, 69, 498-509).—By combination of the Clausius-Clapeyron

equation, the vapour pressure formula of van der Waals, and an equation given by Nernst, the equation

$$-\frac{R\theta}{\lambda} \log(\pi_0/p) \times (1 - p/\pi_0) / M(\theta_0/T - 1),$$

has been deduced, where  $\lambda$  is the molecular heat of vaporisation,  $\theta$ , and  $\pi$  represent the absolute temperature and pressure respectively, and the other symbols have the usual significations. It is shown that this formula is applicable in the neighbourhood of the ordinary boiling point, and the molecular heat of vaporisation can be obtained more accurately by it than by any other formula previously put forward. As it contains no constants which have to be determined empirically, it affords full information as to the deviations from Trouton's rule.

G. S.

**Retrogressive Melting-point Lines. II.** ANDREAS SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 170—177. Compare Abstr., 1909, ii, 971).—Theoretical. Reference is made to the relationships exhibited by the system sodium sulphate-water.

H. M. D.

**Retrogressive Melting-point Lines. III.** ANDREAS SMITS and J. P. TREUP (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 189—192).—The influence of pressure on the form of the melting-point lines is discussed in reference to the experimental data for the binary system ethyl ether-anthraquinone.

H. M. D.

**Retrogressive Vapour Lines. I.** ANDREAS SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 177—182).—A theoretical paper in which the equations for certain equilibrium curves are deduced, and the forms of the curves examined in detail.

H. M. D.

**Three Forms of the Equation of Condition and the Internal Heat of Vaporisation.** THORKELL THORKEELSON (*Physikal. Zeitsch.*, 1911, 12, 633—637).—Three modified forms of the van der Waals' equation are analysed and discussed with reference to the calculation of the internal heat of vaporisation of liquids and of the critical data.

H. M. D.

**Latent Heat of Vaporisation of Liquids.** WILLIAM C. McC. LEWIS (*Phil. Mag.*, 1911, [vi], 21, 268—276).—The author deduces the relationship  $L = -T\alpha/\rho\beta$ , in which  $L$  is the latent heat of vaporisation of a liquid at temperature  $T$ ,  $\rho$  its density,  $\alpha$  its coefficient of expansion with temperature, and  $\beta$  its compressibility coefficient at constant temperature. For normal liquids, the latent heat values obtained from the formula are in approximate agreement with the observed values, but large discrepancies are found in the case of liquids which are presumably associated.

H. M. D.

**Heats of Reaction in Non-aqueous Solutions.** J. HOWARD MATTHEWS (*J. Amer. Chem. Soc.*, 1911, 33, 1291—1309).—The heat of neutralisation of 1 mol. of pyridine by 1 mol. of acetic acid has been measured in a number of different solvents and also in the absence of solvent, the method of measurement being that employed by Richards

and Burgess (Abstr., 1910, ii, 391-390) and Richards and Jesse (Abstr., 1910, ii, 269). In the first set of experiments the pyridine was dissolved in the solvent, and the peracetic acid (not in solution) was run into this solution. The weight of the solvent was kept constant (—96.4 grams) for all the different solvents. The observed heat effects, expressed in calories, for the different solvents were as follows: acetone, 2100.6; water, 1758.0; benzene, 2168.3; carbon tetrachloride, 2177.5; nitrobenzene, 2305.4; carbon disulphide, 2055.6; ethyl acetate, 2263.6; methyl alcohol, 1155.4; ethyl alcohol, 1253.4; isamyl alcohol, 1639.6; when no solvent was used the heat effect was 2286.1 cal. Only in one case, namely, nitrobenzene, is the heat evolved greater than when no solvent is present. The value obtained with water as solvent is considerably less than the values for the other solvents, excepting the alcohols, which are not comparable because of esterification. In the case of solvents such as carbon disulphide, benzene, etc., where no side reactions are to be expected, the values obtained are more nearly of the same order as that obtained when no solvent is used.

In the second series of experiments both the acid and base were dissolved in the solvent before neutralisation took place, the concentration of both the acid and base being the same, namely, 1 mol. in 100 grams of solvent. The following heat effects, in calories, were observed: water, 2715.2; acetone, 1794.8; chloroform, 2358.4; carbon tetrachloride, 2210.4; benzene, 2274.6; ethyl acetate, 2140.2. When these figures are corrected for the heat absorbed or evolved in the process of solution of the pyridine acetate formed in the reaction, they become 786.8, 2125.6, 1152.5, 2317.2, 2481.7, and 2376.4 respectively.

It is obvious that the heat liberated varies greatly from solvent to solvent. These considerable differences cannot be explained as being due to any electrolytic dissociation of the acetate, neither are they due to differences in the heats of solution of the acetate in the different solvents. The chemical nature of the solvents does not seem to give any clue as to the magnitude of the heat of neutralisation, or of the magnitude or sign of the heat of solution of the resulting acetate.

T. S. P.

**Chemical Affinity. V. The Formation of Potassium Lead Sulphate.** J. N. BRONSTED (*Zeitsch. physikal. Chem.*, 1911, 77, 315—330).—The energy relations associated with the formation of the double salt containing lead and potassium sulphates,  $\text{PbSO}_4 \cdot \text{K}_2\text{SO}_4$ , already described by previous observers (compare Barre, Abstr., 1909, ii, 733; Fox, Trans., 1909, 95, 878) have been measured. At  $0^\circ$ , the compound is in equilibrium with a 0.0112 molar solution, at  $22^\circ$  with a 0.0227 molar solution of potassium sulphate.

The affinity, determined by measurements of *E.M.F.* in the usual way, amounts to  $4240 - 2.9(t - 22)$  calories, where  $t$  is the temperature, in good agreement with the same magnitude calculated from the results of cryoscopic measurements, which gave the value 4330 cal. at  $0^\circ$ . From these results the heat of formation of the compound, calculated by means of the Helmholtz formula, amounts to 5090 cal.





Variation with Temperature of the Viscosity of Gases of the Argon Group. MAX KRAMERS (*Zeitsch. Physik.*, 1911, 12, 79—780).—The relationship between Sutherland constants which measure the attraction between the molecules and the absolute critical temperatures referred to by Rankine (Abstr., 1910, ii, 829) has already been pointed out by the author (*Dis.*, Göttingen, 1899).

H. M. D.

Viscosity of Liquid-crystalline Mixtures of *p*-Azoxyanisole and *p*-Azoxyphenetole. \* HANS RICH (*Zeitsch. physikal. Chem.*, 1911, 77, 577—586).—It has been suggested by previous observers that the hardness or elasticity of a metal (compare Faunt and Tamman, Abstr., 1910, ii, 1039) is comparable with the viscosity of a liquid. In order to find whether mixtures of crystalline liquids behave like mixed crystals of solids, the author has measured the density and viscosity of mixtures of *p*-azoxyanisole and *p*-azoxyphenetole at 136°, and finds that, whereas the densities follow the mixture rule, the viscosity of the mixtures is smaller than that calculated according to the mixture rule, the viscosity curve showing a minimum. In this case therefore the expected agreement is not observed, since the curve obtained by plotting the hardness against the composition of a binary system where the components form mixed crystals usually shows a maximum.

G. S.

The Viscosity and Fluidity of Emulsions, Crystalline Liquids, and Colloidal Solutions. \* XI. EUGENE C. BINGHAM and GEORGE F. WHITE (*J. Amer. Chem. Soc.*, 1911, 33, 1257—1275).—From the analogy between viscosity and fluidity, and electrical resistance and conductivity respectively (compare Abstr., 1906, ii, 218), the authors deduce that when liquids are thoroughly mixed, their fluidities will be additive; but if the liquids form an emulsion, a crystalline liquid, or a colloidal solution, or if the mixture is for any other reason incomplete, the fluidity of the mixture will be less than would be the case in a homogeneous solution.

The above conclusions have been verified experimentally by a study of the viscosities of mixtures of phenol and water at various temperatures, especially at those in the neighbourhood of the critical solution temperature. In all the mixtures the fluidity increases with the temperature very rapidly in the neighbourhood of the critical solution temperature, and the various explanations which have been offered to explain this are fully discussed.

T. S. P.

Adsorption Experiments. S. J. LEVITES (*Zeitsch. Chem. Ind. Kolloide*, 1911, April—5).—The adsorption of potassium dichromate and carbamide by bone charcoal, of potassium dichromate and potassium chromium alumina by hide powder, and of potassium dichromate by egg-albumin has been investigated. The data show that the dependence of the adsorption on the concentration of the aqueous solution can be satisfactorily represented by the exponential equation  $x/m = KC^{1/n}$ ,  $n$  is made equal to 2. In very dilute solutions, however, the agreement between the observed and calculated values is not satisfactory.

The data obtained for the absorption of potassium dichromate and sodium sulphate by gelatin show that the adsorbed quantity is nearly proportional to the concentration of the aqueous solution, so that in these cases  $\alpha = 1$ .

The reduction of potassium dichromate in gelatin under the influence of light has also been examined, and numbers are recorded which show the variation of the extent of the reduction during a given period of illumination with the concentration of the adsorbed salt.

H. M. D.

**Determination of the Surface Tension at the Contact of Two Liquids.** (Mlle.) L. VAN DER NOOT (*Bull. Acad. roy. Belg.*, 1911, 493—502).—The method described in a previous paper (this vol., ii, 701) has been applied to the measurement of the tension at the contact surface between two layers of liquid. The apparatus employed consists of a series of U-tubes with limbs of unequal diameter; the lower portion of the tube is occupied by the heavier liquid, and communication between the two portions of the lighter liquid in the two limbs is established by means of a small syphon tube. The differences in level of the contact surfaces in the two limbs are measured, and are then reduced to absolute values by a method of approximation which is described. From these values and the known diameters of the tubes, the capillary constant ( $\alpha^2$ ) for the liquid-liquid contact surface can be calculated. The following values were obtained: water-benzene, 0.389; water-ethyl ether, 0.0840; water-carbon disulphide, 0.287; water-nitrobenzene, 0.220. In every case the pairs of liquids were mutually saturated before being brought into contact. From the capillary constants and the densities of the liquid layers, the liquid-liquid surface tension values are calculated to be: water-benzene, 21.0; water-ethyl ether, 10.0; water-carbon disulphide, 18.4; water-nitrobenzene, 23.0.

H. M. D.

**The Vapour Pressure of Hydrates, Determined from their Equilibria with Aqueous Alcohol.** HARRY W. FOOTE and SAMUEL S. SCHOLZ (*J. Amer. Chem. Soc.*, 1911, 33, 1309—1326).—Several grams of the finely powdered salt were weighed in to a small bottle with a ground-glass stopper. Alcohol was then added from a calibrated pipette, the stopper tightly inserted, and the bottle shaken in a thermostat at 25° for at least two days. When equilibrium had been attained, the compositions of the liquid and solid phases were determined. Only those salts were chosen which were practically insoluble in alcohol.

To find the pressure of aqueous vapour in equilibrium with a given solution of alcohol (the liquid phase as above determined) the relative proportion of alcohol and water molecules in the vapour was determined by combustion. The vapours from the alcohol at 25° were carried into a combustion furnace by means of a stream of pure, dry air, and the products of combustion collected and weighed. Having thus determined the composition of the vapour, its average molecular weight could be calculated and then used in finding the total pressure from the total pressure of the mixture, using as a factor the mole-

cular % of water in its vapour; the partial pressure of aqueous vapour for the mixture could be calculated.

The following vapour pressures, in mm. of mercury, for various systems at 25° were obtained:  $\text{CuSO}_4 \cdot 3-5\text{H}_2\text{O}$ , 7.0;

$\text{CuSO}_4 \cdot 1-3\text{H}_2\text{O}$ , 4.7;

$\text{CuSO}_4 \cdot 0-1\text{H}_2\text{O}$ , 0.8;  $\text{Na}_2\text{SO}_4 \cdot 0-10\text{H}_2\text{O}$ , 18.2;  $\text{K}_2\text{CO}_3 \cdot 0-1.5\text{H}_2\text{O}$ , 1.1;  $\text{CaO} \cdot 0-1\text{H}_2\text{O}$ , 0.8;  $\text{ZnSO}_4 \cdot 6-7\text{H}_2\text{O}$ , 13.6;  $\text{ZnSO}_4 \cdot 1-6\text{H}_2\text{O}$ , 12.8;

$\text{ZnSO}_4 \cdot 0-1\text{H}_2\text{O}$ , 1.0;  $\text{MgSO}_4 \cdot 6-7\text{H}_2\text{O}$ , 11.5;  $\text{MgSO}_4 \cdot 5-6\text{H}_2\text{O}$ , 9.8;

$\text{MgSO}_4 \cdot 4-5\text{H}_2\text{O}$ , 8.8;  $\text{MgSO}_4 \cdot 1-4\text{H}_2\text{O}$ , 4.9;  $\text{MgSO}_4 \cdot 0-1\text{H}_2\text{O}$ , 1.0;

$\text{BaCl}_2 \cdot 1-2\text{H}_2\text{O}$ , 4.8;  $\text{BaCl}_2 \cdot 0-1\text{H}_2\text{O}$ , 2.5;  $\text{Na}_2\text{HPO}_4 \cdot 7-12\text{H}_2\text{O}$ , 18.0;

$\text{Na}_2\text{HPO}_4 \cdot 2-7\text{H}_2\text{O}$ , 12.4;  $\text{Na}_2\text{HPO}_4 \cdot 0-3\text{H}_2\text{O}$ , 8.9.

The above results are given in connexion with the choice of salts as drying agents for organic liquids.

T. S. P.

**Formation of Solid Metallic Solutions by Diffusion in the Solid State.** GIUSEPPE BRUNI and D. MENEGHINI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 927-931. Compare this vol., ii, 703).—When a wire consisting of a gold core on which a layer of copper has been electrolytically deposited is heated at 800° a solid solution of the two metals is completely formed after about one hundred hours. The alloy produced contained 52.5% of gold. Gold and silver similarly treated behave in the same way, the temperature employed being 900° and the resulting alloy containing 62.8% of silver. The extent of the surface of contact of the two metals influences the velocity of diffusion very greatly. A wire was prepared which consisted of sixty thin layers alternately of copper and nickel, and it was found that complete solution had occurred after two hours at 1000°. In this case the change could be detected, not only electrically, but also by means of the microscope.

R. V. S.

**Diffusion Phenomena in [Solutions] of Electrolytes.** B. LINO VANZETTI (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 54-58).—Experiments are described in which simple diffusion leads to the partial separation of the acid and basic constituents of salts. Fresh distilled water, to which neutral litmus or phenolphthalein (faintly reddened) is added in small quantity, is placed in a vertical tube (15-40 cm. long), and a concentrated solution of some salt is then carefully introduced through a capillary tube, reaching to the bottom of the diffusion tube. After some time the colour changes which are observed indicate the separation of acid and base by diffusion. Positive results were obtained with ferric chloride, copper sulphate silver sulphate, potassium chloride, sodium chloride, ammonium chloride, aluminium sulphate, and zinc chloride. In each case the changes observed are described in detail. Although the presence of an indicator seems to modify the results which are obtained in certain cases, blank experiments without indicator show that this influence is of secondary importance.

H. M. D.

**Preponderating Role of Two Electrostatic Factors in the Osmosis of Solutions of Electrolytes.** Normal Osmotic Movements. PIERRE GIRARD (*Compt. rend.*, 1911, 153, 401-404).—Certain

abnormal results in biological experiments on osmosis are explained by supposing that the direction of osmosis depends, not on relative osmotic pressures, but almost exclusively on two electrostatic factors, the sign of the walls of the capillaries composing the septum and the orientation of the active field by which is understood the sum of the difference in potential of the liquid couple, and that corresponding with the polarisation of the septum (Abstr., 1908, ii, 456). Loeb's experiments on the change in volume of the muscles of frogs when immersed in salt solutions are explicable on this theory. Similar anomalies have been realised *in vitro*. Two isotonic solutions, one containing an electrolyte, separated by a membrane, remained in equilibrium until the difference in potential was established, when osmosis occurred in a direction depending on the sign of the charge on the septum, and the orientation of the field; when these were reversed osmosis proceeded in the opposite direction.

W. O. W.

**Proof of the Applicability of Boyle's and Gay-Lussac's Laws to Emulsions.** B. ILYIN (*J. Russ. Phys. Chem. Soc.*, 1911, 43, *Phys. Part*, 134-142).—The author has applied the theoretical considerations and experimental methods of von Smoluchowski (*Ann. Physik*, 1908, [iv], 25, 205) and Svedberg (Abstr., 1910, ii, 773) to the examination of emulsions of gamboge in water of definite concentrations.

The results show that, within the limits of experimental error, variations of concentration in emulsions follow the theoretical laws, and that, for the concentrations employed, the ratio  $\beta/\beta_0$  (compare Svedberg, *loc. cit.*) approximates to unity, or, in other words, the motion of any one particle is independent of the motions of the remaining particles.

T. H. P.

**Certain Objections Recently Raised by A. Colson Against the Ionic Theory.** GEORGES URBAIN (*Bull. Soc. chim.*, 1911, [iv], 9, 753-758).—The author criticises the objections to the ionic theory which have been made from time to time by Colson on the basis of the properties of solutions of the green chromium sulphates (compare Abstr., 1908, ii, 45).

H. M. D.

**Properties of Salt Solutions in Relation to the Ionic Theory.** II. **Electrical Transference Numbers.** ARTHUR A. NOYES and K. G. FALK (*J. Amer. Chem. Soc.*, 1911, 33, 1436-1460. Compare Abstr., 1910, ii, 929).—In the theoretical part of this paper, the theory of transference numbers is fully discussed, taking into account the solvation of the solute and transport of the solvent from one electrode to the other (compare Lewis, Abstr., 1910, ii, 683). A review is then given of previous investigations on transference numbers, and the results of these investigations are collated. The transference numbers obtained by three different methods, namely, the gravimetric, moving-boundary, and conductivity methods, are then carefully compared. At 18° the values obtained by the first two methods are concordant within about 1% for hydrochloric, nitric and sulphuric acids, potassium chloride and sulphate, and ammonium chloride, but for other substances

the gravimetric method gives much higher values (2.5-3%) than the moving-boundary method. The conductivity method also gives values smaller by 1-3% than those of the moving-boundary method for uni-univalent salts. The authors are of the opinion that the moving-boundary method requires further investigation before trust can be placed in the values obtained by it.

In the case of almost all uni-univalent substances the values obtained by the conductivity method at zero concentration agree within about 1% with those obtained by the gravimetric method at 0.005 to 0.02  $N$ . The agreement between these two methods falls outside the experimental error in the case of uni-bivalent salts.

In the last section of the paper the change of the transference number with the concentration and temperature is discussed. With respect to the latter factor, the general statement may be made that the transference number invariably decreases with rising temperature if it is larger than  $600 \times 10^{-5}$  and increases if smaller than this quantity.

T. S. P.

The Laws of "Concentrated" Solutions. II. The Estimation of the Degree of Ionisation of Electrolytes in Moderately Concentrated Solutions. EDWARD W. WAHNBURN (*J. Amer. Chem. Soc.*, 1911, 33, 1461-1478. Compare Abstr., 1910, ii, 1044).—It is pointed out that in calculating the degree of ionisation of an electrolyte by the conductivity method, the neglect of the viscosity effect may produce errors as high as 7 and 8%, even at such low concentrations as 0.1  $N$ , and for such simple electrolytes as uni-univalent salts.

From a consideration of the experiments of Johnston (Abstr., 1909, ii, 854) and Green (Trans., 1908, 93, 2049), the author proposes the relation  $\Lambda = kf^m$  as a basis for applying the viscosity correction in calculating the degree of ionisation of univalent salts, up to a concentration of one equivalent per litre, at least.  $\Lambda$  is the equivalent conductivity of an ion,  $f$  is the fluidity of the solution,  $m$  is a constant not far from unity and dependent chiefly on the nature of the ion, and  $k$  is a constant. This relation gives very good results when applied to Green's figures,  $m$  being given the value 0.94.

From the above relation it may be deduced that the degree of ionisation is given by the expression  $\gamma = \Lambda/\Lambda_0(\eta/\eta_0)^m$ , and examples are given illustrating the results obtained with this equation, and methods for determining the fluidity exponent  $m$  are discussed.

The relation  $\Lambda = kf^m$  leads to the following expression for the true transference number,  $n_A$ , of an ion  $A$  in any solution:

$$n_A = n_{A_0}(\eta/\eta_0)^{m_A - m}$$

$n_{A_0}$  is the transference number at infinite dilution in pure water,  $(\eta/\eta_0)$  the relative viscosity of the solution, and  $m_A$  and  $m$  are the fluidity exponents for the ion and for the salt respectively. Values calculated from this equation are compared with those determined experimentally in the case of potassium, sodium, and lithium chlorides. There is very good agreement in the case of potassium chloride; in the case of the other two salts the change of the transference number

with the increase of viscosity is in the right direction, but is not large enough.

The above relations do not hold in the case of acids and alkalis, and the equation  $\frac{\kappa}{\Lambda_0} = \frac{p}{p_0}$  is suggested for the degree of ionisation ( $\gamma$ ),  $\Lambda$  being the equivalent conductivity of the solution, above which the vapour pressure of the water is  $p$ , whilst  $\Lambda_0$  is the equivalent conductivity of the electrolyte at infinite dilution to which a suitable non-electrolyte has been added, so as to give it the same viscosity and the same vapour pressure,  $p$ , as the first solution.

T. S. P.

**Influence of Pressure and Temperature on the Electrolytic Conductivity of Solutions.** FRIEDRICH KÖRBER (*Zeitsch. physikal. Chem.*, 1911, 77, 420—422).—The claim for priority made by LUSSANA (this vol., ii, 462) is not valid.

G. S.

**Conductivity and Viscosity in Mixed Solvents Containing Glycerol.** J. SAM GUY and HARRY C. JONES (*Amer. Chem. J.*, 1911, 46, 131—197). Compare Jones and Schmidt, Abstr., 1909, 35, 717.—The molecular conductivities in glycerol solution of the following salts have been measured at dilutions varying from 10 to 1600 litres, and at temperatures of 25°, 35°, and 45°: potassium nitrate, chloride and bromide, sodium chloride, bromide, iodide and nitrate, ammonium chloride, bromide and nitrate, barium chloride, bromide and nitrate, calcium bromide, strontium bromide and nitrate, and cobalt chloride and bromide. At 55°, 65°, and 75°, the molecular conductivities in glycerol solution of the following salts were determined: potassium chloride and bromide, sodium bromide and iodide, ammonium nitrate, strontium chloride, barium nitrate, and cobalt chloride and bromide. The molecular conductivities at 25°, 35°, and 45° of potassium chloride, sodium nitrate, and ammonium bromide in aqueous ethyl, alcoholic and methyl-alcoholic solutions containing respectively 25, 50, and 75% of glycerol were also measured, of strontium chloride in aqueous solutions containing 25, 50, and 75% of glycerol, and of ammonium bromide in methyl- and ethyl-alcoholic solution. In addition to the above, the viscosities and fluidities of the above solutions were determined at the respective temperatures.

The conclusions drawn from the results obtained are as follows: Glycerol forms mixtures with water, methyl alcohol, and ethyl alcohol, the properties of which are not additive. The curves representing fluidity and conductivity are very similar to one another over the range of temperature from 25° to 75°. Salts which have the highest power of solvation show the greatest temperature-coefficients of conductivity, and these are greater in the more dilute solutions. In mixed solvents containing glycerol, with water, ethyl and methyl alcohols, the curves representing conductivity and fluidity are strikingly analogous. The molecular conductivities of ternary electrolytes in glycerol at low dilutions are usually smaller than those of binary electrolytes under the same conditions, while at high dilutions the reverse is generally true. While the majority of the salts studied increase the viscosity of glycerol, certain salts of rubidium and ammonium lower its viscosity,

a phenomenon which is most readily explained by the hypothesis of Jones and Yeasay (Abstr., 1908, ii, 257, 260). It is probable that glycerolates exist in the various solutions.

T. S. P.

**The Conductivity and Ionisation of a Penta- and a Hexa-ionic Salt.** ARTHUR A. NOYES and ROBERT H. LOMBARD (*J. Amer. Chem. Soc.*, 1911, 33, 1423—1436. Compare Abstr., 1909, ii, 864).—The authors give the results of measurements at 0°, 25°, and 50° of the molecular conductivity ( $\mu$ ), viscosity ( $\eta$ ), and density of dilute solutions of the tetrasodium and pentasodium salts of benzenepentacarboxylic acid; also values of their molecular conductivity ( $\mu_0$ ) at zero concentration obtained by graphical extrapolation, and values (calculated from these data) of the ratio  $\mu\eta/\mu_0\eta_0$ , which expresses the ionisation ( $\gamma$ ) of the salts, if it be assumed that intermediate ions are not present.

The following principles, derived from the study of salts of smaller valence-products, are shown to be applicable to these two salts. (1) The exponent  $n$  in the function  $C(1-\gamma) = K(C\gamma)^n$ , which expresses the change of ionisation with the concentration, has approximately the same value ( $1.50 \pm 0.05$  at concentrations below  $0.02N$ ) whatever be the number of ions into which the salt dissociates, instead of a value equal to this number of ions, as would be required by the law of mass action. As with salts of smaller valence products, the value which has to be given to  $n$  is smaller at higher concentrations, it being 1.20 for the concentration interval 0.01 to  $0.1N$ . (2) The ionisation of the tetrasodium salt is substantially identical with that of potassium ferrocyanide, a salt of the same valence type. (3) The non-ionised fraction at a given molecular concentration is roughly proportional to the product of the valencies of their ions; thus in a 0.05 molecular solution the non-ionised fraction is  $4 \times 13 = 52\%$  for the tetrasodium salt, and  $5 \times 12 = 60\%$  for the pentasodium salt, whilst the average values previously obtained are 13.5 for uni-univalent,  $2 \times 14$  for uni-bivalent, and  $3 \times 13$  for uni-tervalent salts. (4) Increase in temperature causes only a slight decrease in ionisation of these salts. Thus the change between 0° and 25° is scarcely appreciable, and that between 25° and 50° amounts to 1.5—2% of the ionisation value in 0.05 molecular solution. At 25° and 50°, the molecular conductivity of the quinquevalent ion  $(C_{11}H_9O_{10})^V$  is 1.5 times that of the quadri-valent ion  $(C_{11}H_7O_{10})^{IV}$ , whilst if these ions met with the same frictional resistance the larger charge on the former ion would cause its molecular conductivity to be  $5^{3/4}/4^3 = 1.56$  times that of the latter ion.

The conductivity of benzenepentacarboxylic acid itself was measured at 25° between the concentrations 0.0006 to 0.02 molecular, and it is shown to be a moderately strong acid with respect to both its first and second hydrogens.

T. S. P.

**The Hydrolysis of Iodine and of Bromine. A Correction.** WILLIAM G. BRAY and E. L. CONNOLLY (*J. Amer. Chem. Soc.*, 1911, 33, 1485—1487).—In the previous paper (Abstr., 1910, ii, 819) the authors have omitted to allow for the presence of tri-iodide and

tri-bromide when calculating the concentrations of the iodide and bromide ions. After making the necessary corrections, the values of the constants are found to be  $(\text{H}^+)(\text{I}^-)(\text{HIO})/(\text{I}_2) = 0.3 \times 10^{-12}$  and  $(\text{H}^+)(\text{Br}^-)(\text{HBrO})/(\text{Br}_2) = 5.2 \times 10^{-9}$ .

T. S. P.

**Citrophosphate Solutions. I. Homogeneous Equilibrium in Aqueous Solution Studied by the Cryoscopic Method.** U. PAROLONGO (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 812—818).—The author has carried out a series of cryoscopic determinations with solutions of citric acid, of diammonium citrate, and of mixtures of these substances with mono-, di-, and tri-calcium phosphates. Although no general conclusions are drawn from the results hitherto obtained, yet they do not yield any indication of the formation of complex ions from the citric and phosphoric acids, which has been supposed to take place by some authors (compare Barillé, *Abstr.*, 1908, ii, 496; Quartaroli, *this vol.*, i, 176). The indications are more in accord with the occurrence of double decomposition (compare Grupe and Tollens, *Abstr.*, 1880, 825; Zulkowski and Cedivoda, *Abstr.*, 1903, ii, 451).

R. V. S.

**The Mechanical Stimulus to Crystallisation. II.** S. W. YOUNG and R. J. CROSS (*J. Amer. Chem. Soc.*, 1911, 33, 1375—1388. Compare *this vol.*, ii, 261).—Observations have been made of the freezing point of water containing quartz particles of different sizes in suspension and stirred by the passage of hydrogen at a uniform rate. Assuming that the effect of foreign particles on the freezing point is entirely a kinetic one, and that the stimulus they offer to crystallisation is of an entirely mechanical character, certain conclusions were drawn and tested by experiment.

(1) *The Effect of the Mass of the Particle.*—A liquid charged with particles of large mass should permit of less supercooling than the same liquid charged with particles of small mass, since the disturbance produced by impact of two particles would be proportional to their masses. The experiments confirmed this, the masses of the particles varying from 0.000007 mg. to 0.002 mg.

(2) *The Effect of the Number of Particles.*—At low concentrations the results should be erratic and the amount of supercooling large, since the chances of impact between any two particles occurring within a given interval of time will be relatively small. As the concentrations of the particles increase, the average supercooling should become less, and the results more uniform. When a certain concentration is reached, further increase over a considerable range should not affect the result. The experiments confirmed the above conclusions.

(3) *The Effect of Variations in the Viscosity of the Liquid.*—Increase in viscosity of the liquid will affect the smaller particles more than the larger ones, so that to reach the constant maximum effect, there will be required a considerably greater number of small particles than of large ones. Also, increase in viscosity of the water should protect it against the crystallisation stimulus of foreign particles, and this effect should be greater for small particles than large ones.



Experiments in which gelatin was added to the water were in agreement with the above conclusions.

The above principles are used to explain the conduct of supercooled liquids at rest with respect to their spontaneous crystallization, special reference being made to the work of LANGE (Abstr., 1903, ii, 469) and LAIMANN (Abstr., 1898, ii, 330).  
T. S. P.

**Ultra-microscopic Observations.** CARL THOMAS (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 19—20).—The ultra-microscopic appearance of suspensions of finely-divided coloured substances in water is described, and the whitish appearance presented by particles of gold, platinum, Prussian-blue, and other substances under certain conditions is attributed to the particular size of the particles. This particular size of particle which can thus be identified in a simple optical manner is regarded as a transition stage between the colloidal and suspensoidal conditions.  
H. M. D.

**The Structure of Ultra-microscopic Particles.** THE SVEDBERG and KATSUNO INOUE (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 49—53).—Measurements have been made of the velocity of the Brownian motion of gold particles of different sizes. The colloidal solutions of gold were obtained in three different ways: (1) by the direct reducing action of hydrogen peroxide or hydrazine; (2) by Zeigmondy's germination method, or (3) by the aggregation method, according to which acid was added to the gold hydrosol obtained by the reducing action of phosphorus.

In the case of the small-sized particles of gold obtained by the first method, the Brownian motion is in good agreement with that calculated from Einstein's formula. For the same sized particles obtained by either of the other methods, the agreement is not satisfactory. In the case of larger particles, still greater deviations are found, the extent of the deviation being approximately the same whatever the method employed in the preparation of the hydrosol.

The observed deviations from the above kinetic equation lead to the conclusion that the larger particles deviate considerably from the spherical form. This deviation may be connected with the aggregation of a number of smaller units to form the larger sized particles.

H. M. D.

**Gelatinisation and Hydration-Capacity.** P. P. VON WEIMANN (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 25—28).—The behaviour of various aqueous salt solutions when rapidly cooled to low temperatures is described and contrasted with the solubility of the salts and their tendency to form crystalline hydrates. The conditions favourable to gelatinisation of such solutions are re-stated.  
H. M. D.

**Properties of Colloidal Systems. II. Adsorption as Preliminary to Chemical Reaction.** WILLIAM M. BAYLISS (*Proc. Roy. Soc.*, 1911, 84, B, 81—98. Compare Abstr., 1909, ii, 27).—If a deep blue colloidal solution of the acid of Congo-red is mixed with a freshly precipitated and well-washed aluminium hydroxide

suspended in water, a dark blue precipitate is obtained, which can be washed by centrifugation and again suspended in water. This colloidal dark blue substance contains aluminium hydroxide, for on warming it is converted into the red aluminium salt. The same change occurs very slowly at room temperature. It is supposed that the dark blue colloid represents an adsorption compound containing acid and base which are chemically uncombined. The change in colour from blue to red is indicative of combination between the two constituents. Similar adsorption compounds are formed when the aluminium hydroxide is replaced by zirconium, thorium, or ferric hydroxide.

Observations made with enzymes seem to show that a similar adsorption compound is formed between an enzyme and its substrate as a preliminary to the particular chemical change brought about by the enzyme in question. In particular, it is found that the influence of neutral salts on the enzyme adsorption is quite similar to that observed in cases of ordinary "electrical" adsorption.

Experiments with trypsin and invertase are also described, in which an attempt was made to determine the relationship between the concentration of the enzyme and its activity. Although the connexion between these can be expressed by an exponential formula, it appears that the value of the exponent varies considerably according to circumstances.

H. M. D.

**Properties of Colloidal Systems. III. Osmotic Pressure of Electrolytically-dissociated Colloids.** WILLIAM M. BAYLISS (*Proc. Roy. Soc.*, 1911, *B*, 84, 229-254. Compare Abstr., 1909, ii, 648).—No hydrolytic dissociation is to be detected in solutions of Congo-red, but electrolytic dissociation occurs to a large degree, the dye being 80% ionised in a concentration of 500 litres. \*This value, although large, is less than that of sodium salts of other organic acids of small molecular weight, probably owing to colloidal aggregation of the solutions of the dye-salt.

The osmotic pressure determined experimentally both by direct measurement and by vapour pressure is almost exactly what it would be if no dissociation existed. It should be, however, from one and a-half to three times this value, according to the concentration, an indication of abnormal conditions. The sodium ion is not inactive in the production of osmotic pressure, as shown by the agreement of vapour pressure with direct determinations of the osmotic pressure. Moreover, Chicago-blue, which consists of a single, large non-diffusible anion, like Congo-red, but with four Na ions instead of two, gives double the osmotic pressure of the latter at the same concentration.

The curve expressing the ratio of the conductivity of Congo-red solutions to their osmotic pressure is convex to the axis expressing the conductivity values. The relationship of osmotic pressure and molar concentration is expressed by a straight line.\* The value of the osmotic pressure per unit increase of conductivity rises with concentration, forming an S-shaped curve.

The possibility of aggregated simple ions carrying the sum of the charges of their components is suggested to explain the experimental results.

The distribution of a salt, such as sodium chloride, between the dye solution and water on opposite sides of the membrane is always such that its concentration is greater in the water. This peculiarity of distribution explains the effect of sodium chloride on the osmotic pressure.

If carbon dioxide has access to the outer water of the osmometer, an even approximately constant osmotic pressure cannot be obtained in the case of colloidal salts with a diffusible cation. This is due to an interchange of hydrogen and sodium ions, and hence the escape of the greater part of the sodium from the interior and precipitation of the acid salt.

Congo-red obeys the gas law so far as the effect of temperature on the osmotic pressure of its solutions is concerned. E. F. A.

**The Colour and Degree of Dispersity of Colloidal Solutions.** WOLFGANG OSTWALD (*Koll. Chem. Beihefte*, 1911, 2, 409-485).—Available data showing the relationship between the colour of colloidal solutions and the size of the colloidal particles have been subjected to a detailed examination. The colloidal substances involved are gold, silver, platinum, and other metals of the platinum series, mercury, copper, selenium, tellurium, the alkali metals, sulphur, iodine, metallic sulphides and oxides, and organic compounds.

From this comparison it appears that, in general, the absorption maximum is displaced in the direction of smaller wave-lengths as the degree of dispersity of the colloid increases. An apparent exception is found in the case of solutions of iodine in different organic solvents, but this is attributed to chemical changes in the nature of the disperse phase resulting from the combination of the iodine with the solvent to form disperse aggregates, the nature of which is dependent upon the nature of the solvent, the concentration, and the temperature. True colloidal solutions of iodine can only be obtained in presence of a protective colloid like starch, and in these circumstances it appears that the behaviour of iodine is in accordance with the above generalisation.

Various matters which have some bearing on the subject of the paper are discussed incidentally, such as the colour changes involved in the transition from the highly disperse colloidal condition to that represented by molecular disperse systems, and the colour changes exhibited by rock-salt when its temperature is raised. Experimental observations relating to the preparation of violet-blue, blue, green, yellowish-brown, and reddish-brown colloidal solutions of sulphur in glycerol are also described, and the view is put forward that ultramarine represents a solid solution of colloidal sulphur. It is also noted that the behaviour of sulphur is more complex than that of most of the other substances examined, in that it appears to give rise to two series of coloured colloidal solutions. In both these series, however, the variation of colour with the degree of dispersity of the sulphur is in accordance with the above general rule. H. M. D.

**The System Gum Arabic-Gelatin.** F. W. TIEBCKX (*Zeitsch. Chem. Ind. Berlin*, 1911, 2, 61-65. Compare this vol., ii, 378, 591).—Experiments have been made on the coagulation of

solutions containing gelatin and gum arabic, and on the peptisation of the coagulated products. Data are given which show the influence of various acids and salts at different concentrations, of the relative proportions of the gelatin and gum arabic, and of the temperature. It is pointed out that the investigation of a complex colloidal system of this character is of particular interest in connexion with the explanation of the various factors which have an influence on enzyme action, for it is possible that many enzymes may be regarded as complex aggregates comparable with that investigated by the author.

H. M. D.

**Indifferent Points.** JOUGUET (*Compt. rend.*, 1911, 153, 346—349. Compare Saurel, *Abstr.*, 1903, ii, 15).—A theoretical discussion. Given the pressure, temperature, and concentration of a component in one phase only, these are sufficient to define, not a single system, but a class of systems. The indifferent points for such a class are shown to form a continuum dependent on a single variable.

W. O. W.

**Polarimetric Determination of Avidity of Weak Bases in Non-aqueous Solutions.** EBERHARD RIMBACH and H. VOLK (*Zeitsch. physikal. Chem.*, 1911, 77, 385—410. Compare Skraup, *Abstr.*, 1895, ii, 259).—The activity of ammonia and a number of optically inactive fatty and aromatic amines has been determined in solution in methyl and ethyl alcohols by finding the extent to which they displaced cinchonidine from combination as the nitrate. The position of equilibrium was determined by polarimetric measurements. Corrections were applied for the influence of the free inactive base and of the nitrate of the inactive base on the rotation of the cinchonidine and cinchonidine nitrate respectively. In most of the experiments the ethyl alcohol used as solvent contained 97.5 vol. % of alcohol; the methyl alcohol contained 99.5% by weight of pure alcohol.

From the results the dissociation constants of the bases are calculated, and are represented in tabular form; the relative activities are also referred to ammonia as unit. On the whole the relationships between the strength of the bases and their constitution are similar to those observed in aqueous solution. The activity increases on substituting alkyl groups for hydrogen in ammonia. The strength of the bases increases from methylamine to ethylamine, falls to butylamine, and then increases with increasing complexity of the substituting group. In contrast to piperidine, formylpiperidine is a very weak base, as in aqueous solution.

The most marked difference between the results in aqueous and alcoholic solution is that the activity diminishes regularly when the remaining hydrogen atoms in a primary amine are successively displaced by alkyl groups, whereas in aqueous solution dimethylamine is a stronger base than ethylamine or triethylamine. This result appears to support the suggestion of Walker (compare *Abstr.*, 1906, ii, 735) that the abnormal behaviour of the alkylamines in aqueous solution is due to differences of hydration.

G. S.

**The System Hydrogen Sulphide-Water.** O. SCHREFFER (*Zeitsch. physikal. Chem.*, 1911, 12, 190—201. Complete this vol. ii, 264).—The equilibrium relationships of the system hydrogen sulphide-water have been further investigated, and data are recorded showing the composition of the two liquid phases, which are in equilibrium with vapour and the solid compound, at different temperatures. At the quadruple point, the one liquid contains about 1.3 mole % of water, and the other, 5.4 mole % of hydrogen sulphide. From these values it is evident that the region of non-miscibility extends almost completely over the width of the concentration diagram.

Analyses of the solid hydrate have been made, from which the author draws the conclusion that its composition is represented by  $\text{H}_2\text{S} \cdot 5\text{H}_2\text{O}$ . The greater proportion of water indicated by the analyses of previous workers is attributed to the readiness with which water becomes enclosed in the solid hydrate. H. M. D.

**The System Water-Phenol.** ANDREAS SMITS and J. MAARSH (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 192—195).—The behaviour of liquid mixtures of water and phenol when cooled has been investigated, and a freezing-point diagram constructed. From this it appears that a definite compound,  $2\text{C}_6\text{H}_5\text{OH} \cdot \text{H}_2\text{O}$ , is formed, which melts at  $16^\circ$ , as described by Calvert (*Zeitsch. Chem.*, 1865, 1, 530). The inability of Paternò and Ampola (Abstr., 1897, ii, 476) to observe the formation of this compound is probably due to the readiness with which metastable conditions make their appearance. The following significant equilibrium temperatures were determined: solid phenol in metastable equilibrium with two liquid phases,  $1.70^\circ$ ; ice, solid phenol, and liquid,  $1.2^\circ$ ; ice, solid hydrate, and liquid,  $-1.0^\circ$ ; solid hydrate, solid phenol, and liquid,  $15.8^\circ$ ; stable equilibrium between solid phenol and two liquid phases,  $12.2^\circ$ . H. M. D.

**The System Acetaldehyde-Ethyl Alcohol.** H. L. DE LEROU (*Zeitsch. physikal. Chem.*, 1911, 77, 284—314).—The densities, boiling points, heats of reaction, viscosities, refractivities, and melting points of mixtures of ethyl alcohol and acetaldehyde in different proportions have been measured. The results show that under certain conditions two compounds exist containing 1 mol. of aldehyde to 1 and 2 mols. respectively of alcohol. The existence of the first compound is proved by the occurrence of distinct maxima in the curves representing the variation of the different physical properties with composition; the existence of the second compound is shown most definitely by the freezing-point curve.

When acetaldehyde and alcohol are mixed, there is at first a slight cooling effect, and then the temperature gradually rises. It follows that the heat of mixing is negative, whereas the heat of reaction is positive. The latter attains its maximum value when the components are mixed in equivalent proportions, and amounts to about 1000 cal. per mol.

The boiling-point curves were determined at pressures of 9.7, 40, and 70 mm. At the two lower pressures, the form of the curves

indicates the existence of a highly dissociated compound, but at the higher pressures the curves are normal, showing that at the corresponding temperatures the compound is completely dissociated.

In connection with the freezing-point determinations, a very accurate resistance thermometer is described. Acetaldehyde melts at  $-123.3^{\circ}$ , ethyl alcohol at  $-114.9^{\circ}$ .

In the presence of anhydrous copper sulphate, the double compound of alcohol and aldehyde slowly loses water, acetal being formed.

G. S.

The Course of the P.T.-Lines for Constant Concentration in the System Ether-Anthraquinone. ANDREAS SMITS and J. P. TREUB (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 183—188, Compare Abstr., 1909, ii, 987).—The changes which occur in the form of the pressure-temperature curves as the molar proportion of anthraquinone is gradually increased are discussed in detail.

H. M. D.

Influence of Substitution in the Components on the Equilibrium of Binary Solutions. V. Fluorene and Polynitrobenzenes. ROBERT KREMAN [with DISCHENDORFER, FRANKOVIC, HAUSER, HÖNEL, SCHOUZ, and VALENTA] (*Monatsh.*, 1911, 32, 609—617. Compare Abstr., 1906, ii, 268; 1909, ii, 28).—Freezing-point curves of mixtures of fluorene with nitro-compounds show that fluorene does not form compounds with any of the dinitrobenzenes or with 2:4-dinitrotoluene or 2:4-dinitrophenol. On the other hand, trinitrobenzene, trinitrotoluene, and picric acid yield compounds with fluorene, giving rise to maxima on the freezing-point curve. Fluorene resembles benzene and phenanthrene in this respect, whilst naphthalene can also combine with compounds containing two nitro-groups in an ortho-position.

C. H. D.

Homogeneous Allotropy in a Pseudoternary System. The Ternolecular Pseudoternary System Acetaldehyde-Paracetaldehyde-Metacetaldehyde. ANDREAS SMITS and H. L. DE LEEUW (*Zeitsch. physikal. Chem.*, 1911, 77, 269—283).—The equilibrium in the system acetaldehyde-paracetaldehyde-metacetaldehyde has been determined. It is shown that although the equilibria in the homogeneous pseudobinary systems acetaldehyde-metacetaldehyde and paracetaldehyde-metacetaldehyde must be in the region where metacetaldehyde is present in the supersaturated state, at the equilibrium point in the pseudoternary system the mixture is not supersaturated with regard to metacetaldehyde. Further, the pseudoternary equilibrium is a closed one; in other words, the three components are in complete equilibrium with each other. It is shown that these assumptions account for all the observed phenomena. For example, when a homogeneous mixture at its boiling point,  $41.6^{\circ}$ , is suddenly cooled to  $18^{\circ}$ , a little metacetaldehyde separates, showing that all three forms were present at the higher temperature. From the magnitude of the heats of combustion, the conclusion is drawn that the dissociation should be increased by raising the temperature, and this is borne out by the experimental results.

On the basis of these and other observations, the equilibria in the system are represented on a projected space diagram. Metacetaldehyde melts under the pressure of its own vapour at  $246.2^{\circ}$ .

G. S.

**Speed of Propagation of Chemical Reactions.** W. SREENITSKY (*J. Russ. Phys. Chem. Soc.*, 1911, 43, *Phys. Part*, 148—156).—The author has studied the rate at which the reaction

$5\text{H}_2\text{C}_2\text{O}_4 + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 = 10\text{CO}_2 + \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O}$  is propagated through the liquid when one part of the latter is brought into contact with a solution in which the reaction has already taken place, that is, one represented by the right-hand side of the equation, this acting as a catalyst. The catalytic liquid was poured carefully on to the surface of the other solution in a test-tube immersed in a thermostat, and the passage of the reaction down the tube followed by the decolorisation of the liquid.

The rate of propagation is accelerated with lapse of time; in one experiment the vertical distances covered by the reaction in equal successive intervals of time being, 0.5, 0.6, 0.75, 1.0, 1.5, and 2.5 mm.

The rate of propagation of the reaction diminishes markedly with increase in the diameter of the tube, for example, from 4.5 mm. per ten minutes in a 3 mm. tube to 1.6 mm. for a 9.5 mm. tube and to 1.4 mm. for a 14.5 or 30 mm. tube. The conclusion is drawn that the adsorption of the walls of the tubes has a decided influence on the propagation.

Increasing amounts of quinol cause an increase of the rate of propagation, represented by a quadratic parabola with the axis of velocity of propagation as its axis. The rate of propagation is proportional to the concentration of the reacting solution, and is increasingly accelerated with rise of temperature; for example, 0.3 mm. at  $16.4^{\circ}$ , 0.4 at  $17.8^{\circ}$ , 0.7 at  $20^{\circ}$ , 1.2 at  $22^{\circ}$ , and 1.9 at  $25^{\circ}$ .

T. H. P.

**Theory of Platinum Catalysis with Reference to the Oxidation of Hydrogen by Sulphuric Acid.** JAROSLAV MILBAUER (*Zeitsch. physikal. Chem.*, 1911, 77, 380—384).—The effect of platinum in different forms on the rate of oxidation of hydrogen by sulphuric acid at  $174^{\circ}$  has been determined. The measurements were made by the method already described (*Abstr.*, 1907, ii, 252). The results show that the maximum catalytic effect is obtained when the sulphuric acid is saturated (not supersaturated) with a soluble platinum salt, probably platinum sulphate. The saturation occurs most readily when the platinum is used in the form of platinum-black. The reaction is retarded to some extent by arsenious oxide.

G. S.

**Action of Acids on the Catalytic Oxidation of Phenols by Ferric Salts.** H. COLIN and A. SÉNÉCHAL (*Compt. rend.*, 1911, 153, 282—283).—The formation of complex ferric compounds referred to in a previous communication (this vol., ii, 795) cannot be the only cause of the retarding action exerted by organic acids on artificial

peroxydase systems, since addition of sugars, glycerol, or acetylacetone has little effect on the rate of oxidation of quinol by such systems.

W. O. W.

**Grading of the Intensity in the Properties of Chemical Compounds and Additive Products.** BASIL B. KURILOFF (*Chem. Zeit.*, 1911, 35, 1005).—A chemical compound is characterised by a large number of properties, which, however, can be referred to comparatively few types. One series of properties is necessitated by the law of constant proportions, another by the valency of the elements, a third by the law of mass action (for example, constant dissociation pressure, definite solubility, etc.), and, finally, a fourth by the phase rule. A typical chemical compound possesses the properties of all the above classes, but additive products do not necessarily belong to all four classes.

In the light of the above principles, the author shows how various compounds and additive products can be classified.

T. S. P.

**Ionogenic Atomic Groups and Atoms.** OSCAR HINSEBERG (*J. pr. Chem.*, 1911, [ii], 84, 169—193).—This paper contains an extension of the views of Vorländer (Abstr., 1899, i, 309, 312; ii, 250; 1901, ii, 444; 1902, ii, 250) and Henrich (Abstr., 1899, i, 469, 794; 1900, i, 429) on the nature of radicles. In developing his ideas, the author was guided by the difference in the activity of the extra-nuclear hydrogen atoms of benzaldehyde, benzoic acid, and perbenzoic acid. Whilst the hydrogen atom in benzaldehyde is very reactive but not ionisable, that of benzoic acid, although very readily ionised, shows little chemical activity. In the case of perbenzoic acid, the hydrogen atom is neither reactive nor ionisable. From these considerations the conclusion is drawn that the carbonyl group exerts a two-fold influence on hydrogen atoms in the molecule; firstly, a "reactivating" influence, as in the case of benzaldehyde, and, secondly, an acidifying action, which is restricted to hydrogen atoms in the  $\beta$ -position. This double influence is not confined to the carbonyl group, but is shared by all unsaturated groups, for example,  $O:S:O$ ,  $O:P:O$ ,  $CN$ ,  $\cdot NO$ . According to the author, the reactivating influence is due to intramolecular attractions and repulsions. The acidifying or ionogenic action, on the other hand, is a special characteristic of unsaturated groupings, and is confined in all cases to atoms in the  $\beta$ -position. All unsaturated groups and atoms causing ionisation of other atoms or groups in the  $\beta$ -position are termed ionogens of the second order; the strongly negative elements, such as the halogens and sulphur, are ionogens of the first order, for these elements bring about the ionisation of atoms (hydrogen or metals) only when in direct combination with them.

The author further distinguishes between negative and positive ionogenic radicles and atoms; negative ionogens give rise to acids; positive ionogens to bases.

Chlorine is an ionogen of the first order, and therefore should have no effect on atoms not in direct combination with it. A comparison



on the other hand, in acids and chloroacetic acid shows, however, that the chlorine atom exerts a strongly negative influence on the reactivity of the hydrogen. This is referred to the hydrogen atom being bound to the simultaneous inductive influence of the carbonyl group.

Atoms or groups of this kind which intensify or weaken an ionogenic valency already present in the molecule are termed "commutating" atoms or groups. The commutating effect of the sulphur atom affords an explanation of the greater reactivity of the methylene hydrogen atoms in ethyl thiocetate  $S(OH_2CO_2Et)_2$ , as compared with the methyl hydrogen atoms of ethyl acetate.

The basic properties of triphenylcarbinol, diaryl ketone, and of the iodoso- and iodonium compounds are referred to the presence of the vinylene group,  $\cdot CH:CH \cdot$ , which functions as a positive ionogen of the second order when attached to a carbon or iodine atom.

*o*-Thiocinnamic acid,  $S(CHPh:C-CO_2H)_2$ , prepared by condensing ethyl thioacetate with benzaldehyde by means of methyl-alcoholic sodium methoxide, crystallises in small, colourless needles, m. p.  $223-230^\circ$  (decomp.). F. B.

Dr. Johnstone Stoney's Logarithmic Law of Atomic Weights. LORD RAYLEIGH (*Proc. Roy. Soc.*, 1911, **4**, 85, 471-473).—Extracts are given from a paper communicated by Dr. Stoney to the Royal Society in 1888, and published in part in *Proc. Roy. Soc.*, 1888, **44**, 115.

By taking a series of spheres the volumes of which are proportional to the atomic weights of the elements, and using the radii of these spheres as radii vectors of a polar diagram, a curve is obtained which closely resembles the positive branch of the logarithmic spiral of the second order corresponding with the equation  $r = k \log(q\theta)$ . The author claims that this spiral affords the same information as a Mendeleeff table, and, in addition, furnishes an intelligible representation of the atomic weights.

The absence of elements on a particular sesqui-radius is referred to, and the vacant places pointed out are now occupied by the since-discovered inert gases. In Lord Rayleigh's opinion, this anticipation goes far to justify the high claims made for the diagram by the author.

H. M. D.

The Significance of the Periodic Law. FERNANDO SANFORD (*J. Amer. Chem. Soc.*, 1911, **33**, 1349-1353).—Since the disintegration products of uranium seem to fall into their proper positions in the periodic series, it would seem to follow that the other elements of these groups must in the same way be formed by adding alpha particles and electrons to elements of lower atomic weight. The atomic weights of successive elements do not, however, increase by four or multiples of four, and this difficulty is largely overcome for a considerable part of the series, by assuming two parallel lines of development, one line starting from helium (H, C, and O) and one from lithium (B, N, and F). The two series have, in fact, long been separated on the basis of their valency, the elements of the helium series having zero valency valencies, whilst the elements of the lithium series have odd

valences. They have likewise been separated on the basis of their spectra. The elements of the helium series having their spectral series made up of single lines or groups of three, whilst the elements of the lithium series have their spectral lines arranged in pairs.

The author then discusses a possible cause of radioactivity, and the possibility of artificially changing one element into another, based on the idea that as the electropositive charges on the elements increase, their hold upon the  $\alpha$ -particles must decrease, and the heavier elements must accordingly become more and more unstable, since the positive charges carried by many of the elements are proportional to the square roots of their atomic weights (Sanford, *Phys. Review*, 1911, 32, 512).

T. S. P.

**A Handy Burette Holder.** NORMAN ROBERTS and F. ALEX. McDermott (*J. Amer. Chem. Soc.*, 1911, 33, 1402—1404).—A piece of board (50 x 8 x 2.2 cm.) is bored, a little in front of the middle, with a row of holes about 2.5 cm. in diameter and 5 cm. between the centres. The holes are then connected with the front of the board by slots about 1.7 cm. wide. The bored holes are filed out so as to be slightly conical, with the base up. Conical corks to fit the holes are then bored with borers slightly smaller than the burette they are to carry, and split longitudinally into two equal parts. When the two halves of the cork are placed round a burette and then wedged in one of the holes, the burette will be held firmly, but at the same time may be easily slid up and down. A further improvement is to cut a shallow groove round the upper end of the cork and place in it two or three light rubber bands, so as to keep the two parts of the cork in position.

The perforated board is supported in a bracket, and then forms a convenient holder for several burettes. It may also be used as a funnel support.

T. S. P.

**An Electrically-heated Sealed Tube Furnace.** RAYMOND C. BENNER (*J. Amer. Chem. Soc.*, 1911, 33, 1402).—The tubes of an ordinary bomb furnace are covered with a layer of thin asbestos paper and then wound, each with 55 feet of No. 22 B.S. asbestos-covered nichrome resistance wire, the winding being rather closer at each end of the tube than in the centre. The space within the box and around the tubes is filled with asbestos fibre and magnesium oxide. The tubes are then connected with the 110 volt circuit, about two amperes flow when they are in parallel, and one ampere when in series, the temperatures attained being respectively about 240° and 440°. When no packing is put in the box, the respective temperatures are about 150° and 250°.

T. S. P.

**Apparatus for Maintaining the Level of a Liquid.** EUGEN NOGA (*Chem. Zeit.*, 1911, 35, 997).—The liquid to be evaporated is contained in a large bottle fitted with a two-hole bung, through the one hole of which passes a siphon tube leading to the bottom of the bottle, and through the other hole passes a short right-angled tube. The siphon tube is connected, by means of rubber tubing, with a vertical tube which opens on to the evaporating dish (or on to a funnel in the

case of filtration), and which is sealed at the upper end, into a wider tube the bottom of which is fixed with the narrow tube. Near the seal the wider tube contains a side-tube which is connected by rubber tubing with the right-angled tube in the bottle.

By means of this arrangement, the level of the liquid in the evaporating dish is automatically maintained constant. T. S. P.

**Automatic Filtering of Solutions by Maintaining a Constant Level.** FR. C. BELLAIN-WÖRSCHWELER (*Chem. Zeit.*, 1911, 35, 880).—The principle of the apparatus is as follows: The liquid to be filtered is contained in a large bottle placed on a shelf. A siphon tube leads from the bottle and opens on a filter funnel placed in the neck of another large bottle. A stopcock is inserted in the siphon tube, and is so regulated that the rate of flow of the liquid on to the filter funnel equals the rate of filtration. T. S. P.

**Improvements in Receivers for Vacuum Distillations.** E. JOHN (*Chem. Zeit.*, 1911, 35, 943).—To an upright rod inserted in a plate base are soldered six pairs of thin metal strips which can be used to hold receivers of any shape and size. This arrangement replaces the ordinary one in the well-known Brühl's receiver, where all the vessels are of the same size and shape. T. S. P.

**Apparatus for Continuous Fractional Distillation.** M. M. TICHOWINSKY (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 806—808).—This apparatus is so constructed that each drop of liquid is virtually distilled separately, the thermometer standing automatically at a definite temperature during the whole of the distillation.

The liquid is placed in a separating funnel which stands on a shelf, and is connected with a tube passing through the stopper in the top of the fractionating column. The latter is filled with metallic beads, these being also placed in the side-tube which carries the thermometer nearly up to the bulb of the latter. The column is fitted to a short-necked round-bottomed flask, which together with the burner and the lower portion of the column is protected from draughts by asbestos.

When a little of the liquid is boiled in the flask, distillation soon sets in, and the thermometer becomes stationary. Fresh liquid is then introduced, drop by drop, into the top of the column. With this procedure, the temperature remains surprisingly constant, and there is no difficulty in obtaining a fraction for every two degrees.

Into such a column, made of Bohemian glass, it is safe to drop cold liquid if the temperature is not above 130°. For higher temperatures the liquid is not dropped, but is passed down a tube open at the bottom and enclosed in a wider tube sealed at the bottom, and provided with a lateral orifice at some distance from the bottom; the liquid thus becomes warmed before it issues through the orifice into the column.

By means of this apparatus, a sample of Grosny light petroleum, b. p. 134—137°, was separated into the following fractions: (1) 110 c.c., b. p. 129—139°,  $D_{20}^{20}$  0.7631; (2) 40 c.c., b. p. 129—130.5°,  $D_{20}^{20}$  0.7634;

(3) 120 c.c. b. p. 132—133°, D<sub>4</sub><sup>19</sup> 0.7661; (4) 173 c.c. b. p. 135—136° D<sub>4</sub><sup>19</sup> 0.7675. Nononaphthene has b. p. 135—136° and D<sub>4</sub><sup>20</sup> 0.7652.

T. H. P.

**New Water Decomposition Apparatus with a Dividing Wall.** KARL WERTZACK (*Chem. Zeit.*, 1911, 35, 943).—Instead of the two separate decomposition tubes of an ordinary Hofmann voltameter, one tube is used with a dividing wall down the centre. At the top of the tube each compartment is provided with a tap, and the bottom of the tube below the partition connects with the levelling tube. The electrodes placed in each compartment just above the bottom of the partition are thus fairly close together, and the electrical resistance of the apparatus is small. Being very compact it is not easily breakable.

T. S. P.

**An Improved Soxhlet Condenser.** OSWALD SILBERRAD (*Chem. News*, 1911, 104, 54).—In order to do away with the cork joint between the top of a Soxhlet extractor and the lower end of the reflux condenser, the author simply inserts a bulbous Walters condenser into the open end of the Soxhlet tube, which is somewhat lengthened for the purpose. This, at the same time, does away with the necessity of clamps, etc., for supporting the condenser.

T. S. P.

**A New Extraction Apparatus.** G. A. QUINCKE (*Zeitsch. Nahr. Genussm.*, 1911, 22, 171—172).—The apparatus consists of a glass cylinder, at the bottom of which is placed a flask containing the solvent; the substance to be extracted is placed in a syphon-vessel fitted above the flask and held in position by means of springs which press against the sides of the cylinder, and a suitable glass condenser fits into the top of the cylinder. The latter is heated by means of a water-, oil-, or sand-bath, according to the boiling point of the solvent employed. The apparatus is readily taken apart for cleaning, and the use of corks or rubber stoppers is rendered unnecessary.

W. P. S.

**Two New Forms of Apparatus for Extraction of Liquids with Organic Solvents.** F. C. TEN DOORNKAAT KOOLMAN (*Biochem. Zeitsch.*, 1911, 34, 481—484).—Both forms are figured, and both are constructed on the principles generally adopted for apparatus of this class. The essential modification of one form consists in the connexion of the apparatus with an air blast, so that the liquid is kept in constant agitation during extraction. In the other form, the liquid to be extracted is kept in a long spiral tube, through which the bubbles of the solvent pass.

S. B. S.

## Inorganic Chemistry.

**Apparatus for the Evolution of Large Quantities of Hydrogen Sulphide and Partial Recovery of the Waste Gases from Precipitation Reactions.** A. GWIGNER (*Chem. Zeit.*, 1911, 35, 891).—The apparatus is similar in principle to that described

by the author for the evolution of hydrogen chloride (Abstr., 1901, ii, 83). The waste gases from precipitation reactions are led up a tube lined with glass beads and down which water trickles, and thereby recovered as hydrogen sulphide water. T. S. P.

**Action of Thionyl Chloride on Metallic Oxides.** GEORGES DARZEN and FRANÇOIS BOURION (*Compt. rend.*, 1911, 153, 270—273. Compare Abstr., 1909, ii, 229; Matignon, Abstr., 1905, ii, 459).—When passed over heated metallic oxides below  $400^{\circ}$ , the vapour of thionyl chloride behaves like the mixture of chlorine and sulphur chloride previously used as a chlorinating agent (Abstr., 1907, ii, 690), producing either the anhydrous chloride, as in the case of thorium oxide, or an oxychloride, as in the case of tungstic oxide. Thionyl chloride is less advantageous in practice than the mixture mentioned, owing to the difficulty in obtaining it free from phosphorus compounds. W. O. W.

**The Reduction of Nitrosylsulphuric Acid by Mercury.** O. WENTZKI (*Zeitsch. angew. Chem.*, 1911, 24, 1468).—Polemical against Divers (this vol., ii, 596). T. S. P.

**Apparatus for the Generation of Carbon Dioxide.** C. PURRMANN and P. VERBECK (*Chem. Zeit.*, 1911, 35, 927—928).—Hydrochloric acid contained in a reservoir of special construction is allowed to run into a bottle filled with acid, causing the same to enter a bottle filled with pieces of marble. The gas evolved first passes through an empty bottle, where it deposits any foam; it then passes through a tall wash-bottle containing, besides water, a number of pieces of marble to absorb any hydrochloric acid fumes. For full details, the illustration in the original article should be consulted. L. DE K.

**Colloidal Sulphur.** M. RAFFO and J. MANCINI (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 58—61. Compare Abstr., 1908, ii, 683).—The colloidal sulphur obtained by the slow addition of a concentrated solution of sodium thiosulphate to cooled concentrated sulphuric acid has been subjected to dialysis with the object of determining the dependence of the stability of the solution on the presence of sulphuric acid and sodium sulphate. From measurements of the quantities of sulphur, acid, and sodium sulphate present after different periods of dialysis, the authors draw the conclusion that the presence of definite amounts of electrolyte are necessary for the stability of a colloidal sulphur solution of given concentration. As the electrolytes are progressively removed by dialysis, more and more sulphur separates from the solution in amorphous form.

The coagulation of colloidal sulphur by different electrolytes has also been examined. It is found that potassium salts are much more active than the corresponding sodium salts, whilst these are a little less effective than magnesium and zinc salts. H. M. D.

**Reversible Light Reaction of Sulphur.** ALBERT WIGAND (*Zeitsch. physikal. Chem.*, 1911, 77, 423—471. Compare Abstr., 1908, ii, 672; 1909, ii, 228).—When soluble sulphur ( $S_2$ ) is exposed to

light, it changes slowly into insoluble sulphur. It is now shown that the reaction in question is reversible in light, and a true photochemical equilibrium is attained, both in the case of liquid and dissolved sulphur. The position of equilibrium and the rate of change depends on a number of factors, such as the temperature, rate of stirring, nature of solvent, extent of surface exposed to light, etc., and the effect of each of these factors is described in detail.

In most of the experiments, a mercury-vapour lamp was used as the source of illumination. The principal solvents were carbon tetrachloride and benzene. The relative proportions of  $S_8$  and  $S_2$  were determined by evaporating off the solvent in a vacuum, and extracting the soluble  $S_2$  from the residue; after repeating this process twice, the clear solution was evaporated and the  $S_2$  weighed. In the case of liquid sulphur, the position of equilibrium was determined from the results of freezing-point experiments. When liquid or dissolved sulphur is exposed to light, the  $S_2$  first separates in the colloidal form, and this process has been followed (in the case of solutions) by means of the ultra-microscope.

The absorption of light in sulphur solutions and in liquid sulphur was measured by means of the spectrophotometer.

The heat of solution in carbon disulphide, measured with the ice calorimeter, is for rhombic sulphur,  $-12.3$  cal., and for soluble amorphous sulphur,  $-1.0$  cal. per gram. When 1 gram of  $S_8$  is precipitated from a carbon disulphide solution under the influence of light,  $15.8$  cal. are absorbed; when carbon tetrachloride and benzene are used as solvents, rather less energy is absorbed. For the last two solvents it was found that the energy absorbed in the same interval of time is equal to the product of amount of  $S_2$  precipitated and the work done in bringing about the transformation. Of the energy absorbed, about  $0.24\%$  is used up in bringing about the transformation. G. S.

**Relation between the Three Triple Points of Sulphur.** Hugo R. KAUT (Chem. Weekblad, 1911, 8, 643—648).—No striking proof has been put forward of van't Hoff's expression for the relation of the triple points of sulphur  $\frac{Q \rightarrow}{T \rightarrow} - \frac{Q_{rh}}{T_{rh}} + \frac{Q_{mon}}{T_{mon}} = 0$ , in

which  $Q_{rh}$  is the heat of fusion of rhombic sulphur,  $Q_{mon}$  that of monoclinic sulphur,  $Q \rightarrow$  the transition heat of the conversion of the rhombic into the monoclinic form, and  $T_{rh}$ ,  $T_{mon}$ , and  $T \rightarrow$  the corresponding equilibrium temperatures. The author points out that the most recent results support van't Hoff's views. For  $Q \rightarrow$  Brönsted (Abstr., 1906, ii, 339) obtained the value  $3.28$ ; for  $Q_{rh}$  Lewis and Randall's (this vol., ii, 371) value recalculated for the corresponding temperature was  $15.4$ ; for  $Q_{mon}$  the author obtained  $12.1$  by combining the two values, and for  $T \rightarrow$   $273 + 95.6$ ; for  $T_{rh}$  Smith and Holmes (Abstr., 1903, ii, 284) found  $273 + 110.5$ ; and Reicher's (Diss. Amsterdam, 1883) old, hitherto unchecked, value for  $T_{mon}$  was  $273 + 114.5$ . A. J. W.

**Some Alloys of Metals with Silicon and the Density of Alloys.** R. FRILLEY (Rev. de Métallurgie, 1911, 8, 457—559).—A

large number of alloys of different metals with silicon have been prepared, and their densities determined by means of a specific gravity bottle. By plotting the specific volumes against the percentage composition, curves are obtained showing certain discontinuities, which are rendered more obvious by plotting the molecular volumes. The silicides assumed from these results to exist are much more numerous than those indicated by thermal methods. The method is also applied to alloys of copper with aluminium and with tin, and to alloys of cadmium with mercury.

C. H. D.

**The Structure of the Gel of Silicic Acid.** The Theory of Dehydration. RICHARD ZEIGMONDY (*Zeitsch. anorg. Chem.*, 1911, 71, 356—377).—The moist silicic acid gel is transparent, as in the dry, glassy mass obtained on dehydration, but during the evaporation of the water an intermediate stage is passed through, in which the mass is white and opaque. This has been attributed to the porosity of the gel, and the diameter of the pores has been calculated to be  $1-1.5\mu$ . This is improbable in view of the transparency of the gel, and it is now shown by ultramicroscopical investigation of a dry silicic acid gel saturated with benzene that the true size of the particles is very small, and that the observed coarse structure is due to the accumulation of liquid in some parts, separated by air.

The peculiarities of the curves of dehydration obtained by van Bemmelen (*Abstr.*, 1897, ii, 137) may be explained by assuming that the vapour pressure of the retained water is diminished by the presence of fine capillaries. Assuming the capillary formulae to hold for such small dimensions, the diameter of the pores is calculated to be  $5\mu$  for a depression of vapour pressure of 6 mm. The difference between the curves of dehydration and subsequent re-hydration may be explained as caused by the liquid failing to wet the walls completely in the second case, owing to the presence of adsorbed air. The irreversible changes are due to the union of amorphous particles of silica to form larger particles, probably crystalline.

When silicic acid gel is immersed in a hydrosol of silver, ferric hydroxide, benzopurpurine, or carmin, it acts as an ultra-filter, water penetrating into the gel, whilst a layer of colloid is formed on its surface.

C. H. D.

**Determination of the Absolute Value of the Viscosity of Molten Silicates.** CORNELIUS DOELTER and H. SIEK (*Monatsh.*, 1911, 32, 643—653).—The absolute viscosity of molten silicates may be measured by the method employed by Arrdt (*Abstr.*, 1907, ii, 745) for borates and phosphates. A platinum sphere, 6 mm. in diameter, is partly balanced, and the time taken by it to fall through a given distance is measured. Synthetic diopside, melted in a crucible of Manganese, has been used for the preliminary experiments. The specific gravity of the molten mass, which must be known, is determined by weighing the platinum sphere when immersed, and also by the floating method, using meionite, quartz, and anorthite. Diopside

is used as a standard substance for calibrating the

apparatus. The absolute viscosity of diopside, in C.G.S. units, is found to be 106 at 1280°, diminishing rapidly with use of temperature, and reaching 33 at 1300°.

C. H. D.

**The Hydration and Hardening of Cement.** PAUL ROHLAND (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 21—22).—Keisermann's statement (compare Abstr., 1910, ii, 848) that the author regards the hardening of cement as due to the combination of silicic acid with free lime is refuted. In the author's opinion the hardening consists in the formation of solid solutions or adsorption compounds. A microphotograph by Ambrohn, showing the appearance of cement during the hardening process, is given as evidence in support of the colloido-chemical theory of the process.

H. M. D.

**The Melting of Carbon.** O. P. WATTS and C. E. MENDENHALL (*Ann. Physik*, 1911, [iv], 35, 783—789).—The deformation of carbon rods at very high temperatures has been examined in continuation of experiments of La Rosa (Abstr., 1909, ii, 399, and *Ann. Physik*, 1911, [iv], 34, 95). Comparative observations with samples of American and German carbon rods and of Acheson graphite showed that the lowest temperatures at which deformation took place were respectively 1800°, 1900°, and 2150°. The mechanical properties and the effect of applied stress on the heated rods as well as the appearance of slowly and rapidly heated rods in cross section after cooling are described in some detail. From the experiments, the authors draw the conclusion that the observed deformation is due to gradually increasing plasticity of the carbon, and not to the commencement of melting. The changes in the structural appearance are attributed to volatilisation and subsequent condensation.

H. M. D.

**Catalytic Preparation of Ammonia from Compounds Containing Nitrogen and Carbon.** F. SCHREIBER (*Chem. Zeit.*, 1911, 35, 943).—When carbon or carbohydrate compounds containing nitrogen are heated at 350° with hydrated iron oxide, the nitrogen is transformed into ammonia and carbon dioxide is formed. Experiments in which pyridinesulphonic acid, albumin, potassium ferrocyanide, or Prussian-blue were heated at 350° with excess of an ore containing 32.95%  $\text{Fe}_2\text{O}_3$ , 22.07%  $\text{FeO}$ , and 10.83%  $\text{H}_2\text{O}$  showed that 47—73.7% of the total nitrogen was converted into ammonia. When gas from coke ovens and containing 40.4 grams of hydrogen cyanide per 100 cubic metres was led over the iron oxide heated at 350°, 32.7—47.6 grams of ammonia per 100 cubic metres were obtained.

T. S. P.

**The Ratio of the Molecular Weights of Potassium Chlorate and Potassium Chloride.** ARTHUR STÄHLER and FRIEDRICH MEYER (*Zeitsch. anorg. Chem.*, 1911, 71, 378—402).—Potassium chlorate cannot be fused or dried at 350° without slight decomposition. The salt is repeatedly recrystallised, dried at 100°, and weighed. It is then fused in a quartz vessel, and the water evolved is collected and weighed, the weight of the dry potassium chlorate being thus calculated. The salt is then covered with water, and decomposed by means of purified hydrogen chloride at 0°, quartz vessels being used. The mixture of chlorine and chlorine oxides



evolved is condensed by means of a mixture of alcohol and liquid air, a further vessel being cooled directly by liquid air. The water is removed from the decomposition vessel by slow evaporation in a current of dry air, and the residual potassium chloride is then heated to 300–300° and finally fused in a stationary atmosphere of pure nitrogen and cooled in dry air.

The contents of the condensing vessels are dissolved in water and slowly evaporated in a quartz basin. A minute residue, consisting chiefly of potassium perchlorate, is obtained. It is evaporated with pure perchloric acid and weighed. The final results give, as a mean of five determinations, the ratio  $\text{KClO}_4 : \text{KCl} = 4438.19$ . For  $\text{O} = 16$  and  $\text{K} : \text{Cl} = 1.102641$ , this gives  $\text{K} = 39.097 \pm 0.0004$  and  $\text{Cl} = 35.458 \pm 0.0004$ .

C. H. D.

**Deformation in Mimetic Crystals.** PAUL FISCHER (*Jahrb. Min.*, 1911, *Beil.-Bd.*, 32, 1–48).—Crystallographic descriptions are given of the following salts: ammonium sulphate, potassium sulphate, triammonium hydrogen sulphate  $[(\text{NH}_4)_3\text{H}(\text{SO}_4)_2]$ , tripotassium hydrogen sulphate  $[\text{K}_3\text{H}(\text{SO}_4)_2]$ , and potassium chlorate. A detailed study was made of the twin lamination produced by pressure or by changes of temperature. As indicated by changes in the optical properties with increasing temperature, the last three salts are dimorphous.

L. J. S.

**The Liquidus Surface of the Ternary System Composed of the Nitrates of Potassium, Sodium, and Calcium.** ALAN C. W. MENZIES and N. N. DUTT (*J. Amer. Chem. Soc.*, 1911, 33, 1366–1375).—The freezing points of seventy-one different binary and ternary mixtures of the nitrates of potassium, sodium, and calcium have been determined, and from the results the isotherms representing the contour lines of the liquidus surface have been plotted for each 10° interval to 300°, and for each 50° interval above that temperature.

The freezing points of sodium and potassium nitrates were found to be 315.1° and 346.3° respectively. The freezing point of the mixture represented by  $\text{NaNO}_3 \cdot \text{KNO}_3$  was 228.1°; that of the mixture  $\text{NaNO}_3 \cdot \text{Ca}(\text{NO}_3)_2$  was 261° (by interpolation), whereas Maumene (1883) found 235°.

T. S. P.

**Lithium Amalgams.** G. J. SCHUKOFFSKY (*Zeitsch. anorg. Chem.*, 1911, 71, 403–416; *J. Russ. Phys. Chem. Soc.*, 1911, 43, 708–725).—In the preparation of lithium amalgams, the dried lithium is rapidly introduced into an iron vessel containing some mercury. The vessel is closed and heated until combination has taken place, and, after cooling, mercury is added as required. For the thermal analysis, a protecting layer of paraffin, or for higher temperatures eutectic mixtures of potassium and lithium chlorides, m. p. 352°, or of lithium and sodium chlorides, m. p. 312°, are used.

The freezing-point curve indicates the existence of five compounds,  $\text{Li}_2\text{Hg}$ ,  $\text{Li}_3\text{Hg}$ ,  $\text{Li}_4\text{Hg}$ , and  $\text{Li}_5\text{Hg}$ , the formula of the fifth being uncertain, but lies between  $\text{Li}_4\text{Hg}$  and  $\text{Li}_5\text{Hg}$ . The compound  $\text{Li}_5\text{Hg}$

melts at  $300^{\circ}$ , and is represented by a conspicuous maximum on the curve; the other compounds are only indicated by breaks. The compound  $\text{LiHg}_2$  crystallises in cubes, the remaining compounds in needles.

The heat of formation of the amalgams containing from 50 to 75 atomic % Hg has also been determined by comparing the heat of solution in dilute sulphuric acid with that of lithium. The existence of the compounds  $\text{LiHg}_2$  and  $\text{LiHg}_3$  is thus confirmed. The molecular heat of formation of  $\text{LiHg}$  is 20.2 cal.

The behaviour of lithium in its intermetallic compounds approaches that of magnesium rather than of the other alkali metals.

C. H. D.

**The Action of Nitrogen on Lithium Carbide.** SAMUEL A. TUCKER and HERBERT R. MOODY (*J. Amer. Chem. Soc.*, 1911, 33, 1478—1485).—The preparation of lithium carbide in the electric furnace from a mixture of lithium carbonate and carbon is attended with difficulty, owing probably to the small interval of temperature between its formation and decomposition. The best results were obtained with a mixture of 60 parts of lithium carbonate and 48 parts of carbon, to which 4% of manganese dioxide had been added. With a granular carbon furnace, 210 amperes at 18 volts, gradually increasing to 700 amperes at 30 volts after sixteen minutes, were used. The time of heating never exceeded seventeen minutes, otherwise decomposition of the carbide occurred. The product obtained was for the most part black, and the best results gave a carbide content of 53%. Moissan's claim (*Abstr.*, 1896, ii, 419) to have prepared a nearly pure carbide in the electric furnace could not be confirmed.

The carbide product obtained by the authors gave a maximum absorption of nitrogen at about  $925^{\circ}$ , this maximum absorption being reached in about one hour; longer heating decreases the absorption. The most efficient reaction takes place with nitrogen at a pressure of about 50 lbs. to the square inch.

The product obtained by the action of nitrogen on lithium carbide differs considerably from the corresponding calcium product, or "nitrolime," nitrogen being present as cyanamide, dicyanamide, and cyanide. The proportion of nitrogen fixed does not differ greatly from that fixed by calcium carbide, but the time taken to fix it is much less.

T. S. P.

**Constitution of the Compound of Silver Chloride with Ammonia.** JAN STRAUB (*Zeitsch. physikal. Chem.*, 1911, 77, 331—338).—Bodländer and Fittig (*Abstr.*, 1902, ii, 248) have shown that solutions of silver chloride in ammonia contain the silver almost exclusively as the complex  $\text{Ag}(\text{NH}_3)_2\text{Cl}$ , although the solid in contact with the solution has the formula  $2\text{AgCl}\cdot 3\text{NH}_3$ . The author has repeated these measurements in order to find whether under certain conditions the presence of other complexes in solution can be detected, but the results merely serve to confirm those of Bodländer and Fittig. The method of calculating the results is given in detail.

G. S.

**Method for Determining the Homogeneity of the Phase Number of a Substance in Relation to Silver Mercuric Iodide.** HERMAN WERNING (*Zeitsch. physikal. Chem.*, 1911, 77, 587—590).—Silver mercuric iodide,  $\text{Ag}_2\text{HgI}_4$ , alters in colour from yellow to red when the temperature is raised, but there is no sharp transition point, and there is a difference of opinion as to whether the red substance represents the compound itself or a mixture of the components (compare Ostwald, *Lehrbuch* II, 2, 407). The author has settled this point by shaking the solid compound and mercuric iodide with potassium iodide solutions of varying concentrations until equilibrium is reached at a temperature above the transition point, and analysing the mixtures. It was found that there is no relationship between the mercuric iodide and potassium iodide concentration, as should be the case if mercuric iodide is present in the solid in equilibrium with the solution; hence the red substance is a definite compound. G. S.

**Silver Fluoride and Silver Subfluoride.** LUDWIG VANINO and PAULA SACHS (*Zeitsch. anorg. Chem.*, 1911, 50, 623—629).—Historical. The authors agree with Marignac that the formula of hydrated silver fluoride is  $\text{AgF}_2 \cdot \text{H}_2\text{O}$ . The brownish colour of some specimens is not due to metallic silver, but to silver oxide.

The substance supposed to be silver subfluoride is, according to the authors, not a true compound, but a mixture of silver fluoride and silver (and silver oxide) in varying proportions. L. DE K.

**The Extraction of Silver from its Ores by means of Cyanides.** E. KOHN (*Metallurgie*, 1911, 8, 399—404, 421—436, 464—472, 481—492).—In the extraction of silver sulphide by means of potassium cyanide, the reaction  $\text{Ag}_2\text{S} + 6\text{KCN} = 2\text{AgK}_2(\text{CN})_2 + \text{K}_2\text{S}$  occurs, the constants for which have been determined by Lucas (Abstr., 1904, ii, 715). The equilibrium is further complicated by the hydrolysis of the cyanide and the sulphide. Taking this into account, formulae are arrived at from which a three-dimensional diagram is constructed, the co-ordinates of which are the concentrations of KCN, KSH, and Ag respectively. Silver sulphide is only dissolved within a region forming a limited part of the equilibrium surface. It is found, however, that in very dilute solutions (below 0.05N KCN) the reaction is not in accordance with Lucas's equation.

In practice, the quantity of silver dissolved is increased by removal of the alkali sulphide produced, by means of lime in presence of air, or by addition of lead acetate, or, better, of lead oxide. C. H. D.

**The Ternary System Silver-Zinc-Lead. The Theory of the Parkes Process.** ROBERT KREMANN and F. HOFMEIER (*Monatsh.*, 1911, 32, 561—595).—As silver and zinc form four well defined compounds (Petrovsky, Abstr., 1906, ii, 284), whilst lead does not form compounds with either silver or zinc, the ternary system may be broken up into five ternary systems,  $\text{Pb-Zn-Ag}_2\text{Zn}_3$ ;  $\text{Pb-Ag}_2\text{Zn}_3\text{-Ag}_2\text{Zn}_4$ ;  $\text{Pb-Ag}_2\text{Zn}_4\text{-AgZn}$ ;  $\text{Pb-AgZn-Ag}_2\text{Zn}_2$ , and  $\text{Pb-Ag}_2\text{Zn}_2\text{-Ag}$ . On the triangular diagram these systems occupy five triangles having

a common metal. The primary crystallisation of lead is restricted to a very small area, and the ternary eutectic contains about 97.5% of lead, and melts at 306°.

In the technical extraction of silver from lead by the Parkes process, the quantity of zinc added is so small that the region of two immiscible liquid phases is not usually entered. The crystals which separate on cooling are then solid solutions of zinc and the compound  $A_{12}Zn$ . A small proportion of the binary eutectic, of which the other constituent is lead, also separates. Repetition of the process brings the system nearer to the line Pb-Zn, the silver passing almost exclusively into the crystalline phase.

C. H. D.

**Bolognian Stones. III.** LUDWIG VANINO and EMILIE ZUMBUSCH (*J. pr. Chem.*, 1911, [ii], 84, 305—317. Compare Abstr., 1909, ii, 731; 1910, ii, 847).—In the earlier papers it was pointed out that in Bolognian stones exhibiting a marked phosphorescence, only a portion of the barium, strontium, or calcium exists in combination in the form of sulphides. The object of the present communication is to ascertain more exactly the relationship existing between the luminosity of the stones and their sulphur content.

In good calcium stones the total amount of sulphur may vary between 12% and 33%, but with a slightly greater sulphur content the luminosity is considerably impaired. Stones in which polysulphides could not be detected were always found to be feebly luminous. That this lack of phosphorescence is really due to a deficiency of polysulphides is proved by the fact that stones, prepared by igniting calcium sulphate with carbon, and therefore free from polysulphides, are non-luminous. Moreover, whilst the addition of fusible salts and traces of metals to these non-luminous calcium monosulphide stones produces only a very feeble phosphorescence, the addition of a small quantity of sulphur results in the formation of more strongly luminescent stones. The presence of polysulphides thus appears to be essential for the production of good stones, but the amount of sulphur in the form of polysulphides is always comparatively small, varying from  $\frac{1}{2}\%$  to  $2\frac{1}{2}\%$ .

The phosphorescence also depends on the texture of the stones. Those consisting of monosulphides are always obtained in the form of hard, stony, non-luminous or, at most, very feebly luminous masses. Addition of calcium oxide to these monosulphide stones produces a less compact mass, and at the same time a marked increase in their luminosity. The quality of the lime used in the preparation of the stones is also of importance, but no essential difference could be detected in the composition of feebly luminous stones prepared from unsuitable specimens of lime, and stones showing an intense luminescence. Partial replacement of calcium oxide by strontium carbonate or oxide in the preparation of the stones exercises no influence on their sulphur content, although the mixed stones thus obtained are characterised by an intense phosphorescence.

The effect of reducing agents has also been investigated; whilst the addition of 4% of starch is advantageous, larger quantities completely destroy the phosphorescence; good results are also obtained with cane

spark, but not with lamp-black. With respect to the influence of pressure, it is found that the previously observed diminution in the intensity of the luminescence is accompanied by a change in the colour of the stones. When ground in the dark, all stones lose their original colour and acquire a more or less greyish tint. A further change of colour is observed on exposure to light, the stones in this case acquiring a reddish or even a reddish-brown tint. This secondary coloration depends on the metallic content and percentage of sulphur; increase of the latter produces a marked increase in the intensity of the colour. Stones acquiring a strong secondary colour sometimes exhibit very feeble luminosity, so that there appears to be no connexion between the two phenomena.

Admixture of the phosphorescent masses with photo-sensitisers, or exposure to chlorine, ammonia, hydrogen sulphide, and other gases has no effect on their luminosity.

Further attention has also been directed to the influence of metallic salts on the phosphorescence. Addition of silver, gold, or platinum salts, arsenic sulphides, or of coloured substances, such as ultramarine or Thenard's blue, has either little or a deleterious effect on the luminosity. Partial replacement of calcium oxide by calcium tungstate in a mixed strontium-calcium stone produces a magnificent sea-green luminescence.

With stones of high metallic content and simple composition, the time of exposure necessary to excite the maximum luminescence is shorter, and the rate of decay more rapid, than in the case of stones of a low metallic content and complex composition. F. B.

**Transformation of Aragonite into Calcite.** P. N. LARICHTSCHENKO (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 793-803).—The results of previous investigators have shown that between the ordinary temperature and one not lower than corresponds with a red heat, calcite is undoubtedly a more stable form of calcium carbonate than aragonite. But discord exists in regard to the magnitude of the heat-change accompanying the transformation of the latter into the former modification; thus, Favre and Silbermann, whose results are stated by Abegg (*Handbuch der anorg. Chem.*, 1905, II, 2, 155) to be clearly erroneous and are not mentioned by Tammann (*Krystallisieren und Schmelzen*, 1903, 113), found the heat of transformation of aragonite to calcite to be +2.36 Cal. per gram-mol., whilst Le Chatelier (*Abstr.*, 1893, ii, 259) obtained the value -0.300 Cal. per gram-mol. Widely different temperatures have also been given by various authors as that at which the above transformation occurs.

The author has investigated this change by determining calorimetrically the amounts of heat given out on cooling by aragonite and calcite (marble and Iceland spar) heated to various temperatures.

In the case of aragonite, the curve expressing the relation between the amount of heat evolved and the temperature is composed of three portions. In the first (up to about 400°) the curve cannot, by the method used, be distinguished from that for calcite. At 445°, however, a distinct separation occurs, the heat of cooling of aragonite

increasing rapidly until the temperature reaches  $465-470^{\circ}$ . The third portion of the curve again coincides with that for calcite, although above  $600^{\circ}$  there appears to be some divergence.

A sudden change also takes place in the specific gravity of aragonite at about  $465-470^{\circ}$ ; the values of  $D_{15}$  found by the author being as follows:  $16.5^{\circ}$ , 2.9219;  $400^{\circ}$ , 2.9278;  $410^{\circ}$ , 2.9209;  $445^{\circ}$ , 2.9217;  $450^{\circ}$ , 2.9218;  $460^{\circ}$ , 2.9231;  $465^{\circ}$ , 2.9215;  $475^{\circ}$ , 2.7691;  $525^{\circ}$ , 2.7711;  $650^{\circ}$ , 2.7800.

These results show that the turbidity and brittleness of aragonite crystals observed by Boeke (Abstr., 1906, ii, 753) to appear at  $445^{\circ}$  are not connected with the transformation into calcite.

Taking the temperature of the transformation as  $465-470^{\circ}$ , the difference between the heats of cooling of calcite and aragonite gives the value about 2.72 Cals. per gram-mol. for the heat-effect of the change; this number is in fair agreement with that given by Favre and Silbermann (*loc. cit.*).

T. H. P.

**Electrical Conductivity and Hardness of Magnesium-Cadmium Alloys.** G. G. URAZOFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 762-771).—The electrical conductivity and hardness of alloys of magnesium and cadmium confirm Grube's view (Abstr., 1906, ii, 355) that, at the ordinary temperature, these alloys contain two series of solid solutions: (1) of the compound  $\beta\text{-CdMg}$  and (2) of  $\alpha\text{-MgCd}$ , in their components. With the compound  $\alpha\text{-CdMg}$  correspond a maximum of conductivity and a minimum of hardness (compare Schemtschuschny, Abstr., 1906, ii, 539; Kurnakoff and Schemtschuschny, Abstr., 1908, ii, 932; Smirnof and Kurnakoff, Abstr., 1909, ii, 402). The following temperature-coefficients of resistance have been determined: Mg, 0.00438; Cd, 0.00425, and  $\alpha\text{-CdMg}$ , 0.00586.

On addition of cadmium to magnesium, the specific conductivity diminishes rapidly until 20 atom. % Cd is present; this part of the curve corresponds with the formation of solid solutions of  $\beta\text{-CdMg}$  with magnesium. At the 20% Cd point, the conductivity suddenly rises, the curve subsequently falling, rising to a maximum for the composition corresponding with the compound CdMg, then falling again, and rising until the atom. % of cadmium reaches 82.5; this part of the curve corresponds with solid solutions of  $\alpha\text{-MgCd}$  in its components. At 82.5% Cd, the curve exhibits a sudden fall, and then rises rapidly to the pure cadmium point; this branch corresponds with solid solutions of  $\beta\text{-CdMg}$  with cadmium.

As the temperature is raised, the region in which solid solutions of  $\alpha\text{-CdMg}$  exist continually decreases, until at  $255^{\circ}$  it vanishes altogether. At this and higher temperatures, an uninterrupted series of solid solutions of  $\beta\text{-CdMg}$  is formed, and the conductivity curve consists of two continuous branches meeting in a maximum at the  $\beta\text{-CdMg}$  point.

The micro-structures of alloys of various compositions confirm these results.

T. H. P.

**Definite Compounds with Variable Composition of the Solid Phase. I. Electrical Conductivity and Hardness of the System Magnesium-Silver.** WLADIMIR I. SMIRNOFF and NICOLAI S. KURNAKOFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 725-752; *Zeitsch. anorg. Chem.*, 1911, 72, 31-54).—In the first part of this paper the authors discuss the forms of the conductivity and hardness curves of compounds with varying composition of the solid phase and melting (1) without and (2) with decomposition.

The general form of the conductivity curve resembles that of the freezing point curve (compare Schentschuschny, *Abstr.*, 1906, ii, 539), the maximum corresponding with the composition  $MgAg$  being clearly marked. The results show that all the substances formed in the system magnesium-silver show varying composition of the solid phase. The temperature-coefficients of the conductivity are important and characteristic magnitudes, and for the compounds  $MgAg$  and  $Mg_2Ag$  they approximate to the corresponding values for the component metals.

The third part of the paper, dealing with the hardness of these alloys, has been already published (*Abstr.*, 1909, ii, 402).

T. H. P.

**Differences of Potential between Cadmium and Alcoholic Solutions of Some of its Salts.** FREDERICK H. GETMAN (*Amer. Chem. J.*, 1911, 46, 117-130. Compare Jones, *Abstr.*, 1894, ii, 374; Kahlenberg, *Abstr.*, 1899, ii, 624; 1901, ii, 81, and Jones and Smith, *Abstr.*, 1900, ii, 467).—The author has measured the potential at 20° of the cadmium electrode against solutions of cadmium iodide and cadmium chloride in methyl alcohol, ethyl alcohol, and water respectively, the normal calomel electrode being used as the standard. In alcoholic solution the potential becomes more strongly negative (with reference to the solution) as the concentration of the solution increases, whereas in aqueous solution the opposite is the case. When cadmium is immersed in solutions of cadmium iodide in ethyl alcohol of concentrations less than 0.06 molar, there is a reversal of the polarity of the system, and the current flows outside of the cell from cadmium to mercury instead of from mercury to cadmium, as in methyl alcohol and aqueous solutions. The behaviour of the electrode in alcoholic solutions is contrary to what one would expect from Nernst's theory of the voltaic cell, unless the improbable assumption is made that the degree of ionisation increases with dilution more rapidly than the dilution increases, so that at present the theory cannot be extended to non aqueous solutions.

The solution pressure of cadmium is calculated to be  $5.64 \times 10^6$ ,  $1.88 \times 10^6$ , and  $1.64 \times 10^6$  atmos. respectively from measurements on 0.01, 0.05, and 0.1 molar aqueous solutions of cadmium iodide, and  $3.45 \times 10^6$  and  $1.07 \times 10^6$  atmos. from measurements on 0.01 and 0.05 molar aqueous solutions of cadmium chloride. There are no data on which a calculation of the solution pressure of cadmium in the alcohols can be based.

The point measurements showed that cadmium iodide is partly dissociated in both methyl- and ethyl-alcoholic solution. T. S. P.

**Persulphates of Bivalent Metals.** GUISEPPE A. BARRIERI and F. CALZOTARI (*Zeitsch. anorg. Chem.*, 1911, 71, 347—355).—The only persulphates of bivalent metals hitherto prepared are those of barium and lead (Marshall, *Trans.*, 1891, 59, 771). These salts are in general very unstable. It is now found that the persulphates form crystalline compounds with ammonia, pyridine, and hexamethylenetetramine. The last of these compounds furnishes the only means of preparing manganous and cobaltous persulphates (compare this vol., i, 268). The hexamethylenetetramine compounds contain water, and their properties indicate that the central atom is not in contact with molecules of the base, but is surrounded by water molecules.

The ammonia compounds may be prepared by adding a concentrated solution of ammonium persulphate (2 mols.) to a concentrated, strongly ammoniacal solution of the metallic sulphate (1 mol.). The crystalline products are washed with ammonia and dried with filter paper. They lose ammonia readily, and explode on heating or percussion. The following ammine persulphates have been prepared: zinc,  $\text{ZnS}_2\text{O}_8 \cdot 4\text{NH}_3$ ; cadmium,  $\text{CdS}_2\text{O}_8 \cdot 6\text{NH}_3$ ; nickel,  $\text{NiS}_2\text{O}_8 \cdot 6\text{NH}_3$ , and copper,  $\text{CuS}_2\text{O}_8 \cdot 4\text{NH}_3$ .

The following pyridine persulphates have been prepared: zinc,  $\text{ZnS}_2\text{O}_8 \cdot 4\text{C}_5\text{NH}_5$ ; cadmium,  $\text{CdS}_2\text{O}_8 \cdot 4\text{C}_5\text{NH}_5$ ; nickel,  $\text{NiS}_2\text{O}_8 \cdot 4\text{C}_5\text{NH}_5$ , light blue, and copper,  $\text{CuS}_2\text{O}_8 \cdot 4\text{C}_5\text{NH}_5$ , bluish-violet.

The hexamethylenetetramine persulphates are precipitated, separated as rapidly as possible from the mother liquor, and washed with alcohol. The *magnesium*, *manganese*, *cobalt*, and *nickel* salts all have the composition  $\text{MS}_2\text{O}_8 \cdot 8\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_{12}\text{N}_4$ . The manganese and cobalt salts are shown to be isomorphous. The cobalt and nickel salts resemble in colour the ordinary hydrated salts of those metals. C. H. D.

**The Nature of the Transformation of Lead-Tin Alloys in the Solid State.** DOMENICO MAZZOTTO (*Internat. Zeitsch. Metallographie*, 1911, 1, 289—352).—The transformation occurring in solid lead-tin alloys at about  $150^\circ$  has been attributed by Degens (*Abstr.*, 1909, ii, 888) to the formation of a compound of the two metals, and by Rosenhain and Tucker (*Abstr.*, 1908, ii, 1038) to an allotropic change in the solid solution of tin in lead. Cooling curves of the alloys have now been taken after annealing for different periods below, at, or slightly above the eutectic temperature. Mercury is used as a standard of comparison. The conclusion is drawn from the curves that it is unnecessary to assume either combination or allotropic change, the heat developed during cooling being merely due to the separation of tin from solid solution with falling temperature. Annealing increases the saturation of the solid solution. The transformation occurs at  $150^\circ$  in alloys containing 18% Sn or more, but below that temperature at lower concentrations.

Similar transformations are observed in alloys of tin with bismuth, thallium, and cadmium, in all of which solid solutions are formed. C. H. D.

**Action of Seltzer Water on Lead, Tin, and Antimony. Causes of Poisoning by Chemical Alteration.** A. BARILLÉ (*Compt. rend.*, 1911, 153, 351—353).—Alloys of lead or antimony

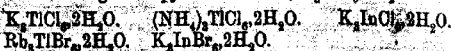


with tin are more soluble in salt water than either metal separately, even when an alloy contains only 0.5% of lead. A litre of Seltzer water gave 0.0966 gram of lead sulphate and 0.0381 gram of stannic acid when allowed to act for six months on the head of a siphon containing 19.47% of lead. An alloy containing 10% of antimony gave 0.153 gram of antimonious oxide after two months. The use of porcelain or silicious linings for siphon heads is recommended.

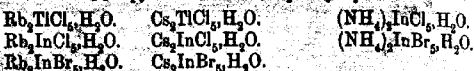
W. O. W.

**Crystallographic (Isomorphous) Relations of Indium and Thallium.** R. C. WALLACE (*Zeitsch. Kryst. Min.*, 1911, 49, 417-454).—Detailed crystallographic determinations were made for several salts in the following isomorphous series:

1. The ditetragonal-bipyramidal series,  $R_3MX_6 \cdot 3H_2O$ :

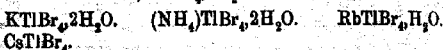


2. The rhombic-bipyramidal series,  $R_3MX_6 \cdot H_2O$ :



Isomorphous with these are  $K_3FeCl_6 \cdot H_2O$  and  $(NH_4)_3FeCl_6 \cdot H_2O$ .

3. The cubic series,  $RMX_4 \cdot 2H_2O$ :



4. The ditetragonal-bipyramidal salt,  $K_3Ti_2Br_9 \cdot 3H_2O$ .

The effect of the various replacements on the crystallographic constants is discussed. The alkalis stand in the order K,  $(NH_4)$ , Rb, Cs, there being very little interval between  $(NH_4)$  and Rb. With Fe, In, Tl, the intervals are approximately proportional to the differences in the atomic weights.

L. J. S.

**Decomposition of the Cerium Earth Double Sulphates with the Alkali Sulphates by Fusion with Charcoal.** PHILIP E. BROWNING and PHILIP L. BLUMENTHAL (*Amer. J. Sci.*, 1911, [iv], 32, 164-166).—One part of the double sulphate is heated with four parts of charcoal in a covered porcelain crucible over a Bunsen flame for about an hour. The mass then dissolves readily in dilute hydrochloric acid with evolution of hydrogen sulphide. From the filtrate the cerium may be recovered by precipitation with oxalic acid and then ignited to oxide.

L. DE K.

**Sulphides of the Rare Earths. II. Lanthanum and Praseodymium Sulphides.** WILHELM BILTZ (*Zeitsch. anorg. Chem.*, 1911, 71, 427-438. Compare Abstr., 1908, ii, 1037).—Like cerium, lanthanum and praseodymium yield normally only trisulphides (Müllmann and Stützel, Abstr., 1900, ii, 142), but higher polysulphides are obtainable.

*Lanthanum disulphide*,  $\text{LaS}_2$ , prepared by heating lanthanum sulphate in hydrogen sulphide at  $580-600^\circ$ , behaves as a polysulphide, and decomposes when more strongly heated at about  $650^\circ$ . A comparison of the heat of solution of the two sulphides in hydrochloric acid gives the result  $4\text{LaS}_2 = 2\text{La}_2\text{S}_3 + \text{S}_2(\text{gas}) - 43.4$  cal. This gives a theoretical dissociation temperature of  $670^\circ$ , about  $100^\circ$  lower than that of cerium disulphide.

The action of hydrogen sulphide on anhydrous praseodymium sulphate only results in the formation of *praseodymium oxy-sulphide*,  $\text{Pr}_2\text{SO}_2$ . Sulphides free from oxygen are only obtained in the presence of some cerium. In the same way, cerium is known to assist the formation of praseodymium peroxide. *Praseodymium disulphide*,  $\text{PrS}_2$ , dissociates at a temperature near that of the lanthanum compound.

C. H. D.

**Thulium.**—I. CHARLES JAMES (*J. Amer. Chem. Soc.*, 1911, 33, 1332—1344. Compare Abstr., 1910, ii, 412).—The best sources for thulium were found to be ytter spar, euxenite, and a columbate, resembling apophyllite, from an island in the north of Norway, and having the following composition:

$\text{Ce}_2\text{O}_3$ (trace $\text{Ta}_2\text{O}_5$ )	$\text{SiO}_2$	$\text{WO}_3, \text{SnO}_2$	$\text{ZrO}_2$	Cu group.	$\text{U}_3\text{O}_8$	$\text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3$
42.42	4.27	0.37	0.41	1.38	1.40	1.55

Yttrium earths.	Cerium earths.	$\text{ThO}_2$	$\text{CaO}$	$\text{MgO}$	Loss on ignition.
39.91	3.57	1.10	1.25	0.07	2.00

The preliminary treatment in the various cases was as follows:

*Euxenite*.—The finely powdered material was evaporated to dryness with excess of sulphuric acid. The residue was powdered, well agitated with water, and the metallic acids allowed to settle, after which the rare earths were precipitated as oxalates from the supernatant fluid.

*Fergusonite and Samarskite*.—These were treated similarly to euxenite, except that potassium sulphate was added to the sulphuric acid so as to increase the temperature. In some cases the hydrofluoric acid method of treatment was adopted.

*Columbates*.—The mineral was first ignited, then powdered, and fused with sodium hydroxide. The cold fusion was made into a mud with water and then heated on the water-bath with hydrochloric acid. The columbic acid, etc., was filtered off, and the rare earths precipitated as oxalates. *Pitrotitanite*, was attacked with hydrochloric acid, filtered, and the rare earths obtained as oxalates. *Ytterspar* (impure Norwegian xenotime) was treated in much the same way as the columbates, while *gadolinite* was decomposed by heating with hydrochloric acid, the rare earths being obtained in the usual way.

The ytterspar earths were converted into the bromates by igniting the oxalates, dissolving in hydrochloric acid, filtering, and reprecipitating as oxalates, which were then converted into the sulphates. The anhydrous sulphates were dissolved in water, and the solution heated on a water-bath with barium bromate. After collecting the barium sulphate, the bromates were fractionally crystallised.

The earths from euxenite, gadolinite, etc., were first subjected to the sodium sulphate treatment, since they contained members of the cerium

group. After separating the insoluble double sulphates, the solution was precipitated with oxalic acid, the oxides obtained, and converted into the bromates in a manner similar to that described for the ytterspar earths.

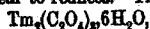
Thulium was then concentrated by fractional crystallisation of the bromates (compare *Abstr.*, 1908, ii. 190, 498), collecting in the fractions between erbium and ytterbium, and being more soluble than erbium. The fractions in which the thulium bands were intense were finally submitted to a long series of recrystallisations, as they consisted mainly of ytterbium and lutecium, with some erbium and traces of scandium. The thulium was gradually concentrated in the fractions next to the least soluble erbium, and when free from erbium the solutions possessed a bluish-green colour. The presence of a little erbium turns the colour yellowish-green, a little more renders it colourless, and further addition changes it to pink. The various colours so obtained were made use of in collecting the fractions. It was found that the thulium fractions did not change in colour, always retaining a greenish tint when in solution.

Other methods of fractionation were tried, but none could be compared with the bromate method.

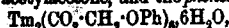
Spectroscopic examination (by Sir William Crookes) of the purest thulium fraction obtained showed it to contain a trace of ytterbium and a very faint trace of calcium.

The results show that the element giving the characteristic absorption bands of thulium cannot be separated into simpler substances. After 15,000 operations the absorption spectrum underwent no change.

The following compounds are described: *Thulium oxide*,  $\text{Tm}_2\text{O}_3$ , prepared by igniting the oxalate, forms a dense white powder with a faint green tint. It gives a carmine glow when carefully made to incandescence. *Thulium hydroxide* is best precipitated by means of ammonium hydroxide. *Thulium bromate*,  $\text{Tm}_2(\text{BrO}_3)_6 \cdot 18\text{H}_2\text{O}$ , was obtained as pale bluish-green, hexagonal prisms from thulium sulphate and barium bromate. *Thulium chloride*,  $\text{Tm}_2\text{Cl}_6 \cdot 14\text{H}_2\text{O}$ , was prepared from the oxide and hydrochloric acid. It forms crystals with a green tint. The *sulphate*,  $\text{Tm}_2(\text{SO}_4)_6 \cdot 8\text{H}_2\text{O}$ , was obtained from the chloride and sulphuric acid by precipitating the solution with alcohol. It loses  $8\text{H}_2\text{O}$  at a temperature near to redness. The *oxalate*,



possesses a greenish tinge. It forms double salts with potassium and ammonium oxalates. *Thulium acetylacetonate*,  $\text{Tm}_2(\text{C}_5\text{H}_7\text{O}_2)_6 \cdot 2\text{H}_2\text{O}$ , was obtained by dissolving the hydroxide in a warm mixture of absolute alcohol and acetylacetone, and the *phenoxycetate*,



from the hydroxide and phenoxycetic acid. *Thulium nitrate*,



was obtained from the oxide and nitric acid.

T. S. P.

**Rare Earth Compounds.** L. A. PRATT and CHARLES JAMES (*J. Amer. Chem. Soc.*, 1911, 33, 1330—1332).—The following compounds were prepared by solution of yttrium oxide in the correspond-

ing acid and evaporation of the solution to dryness. The residue was then dissolved in alcohol and the salt precipitated with ether.

*Yttrium methylsulphonate*,  $(\text{MeSO}_2\cdot\text{O})_3\text{Y}\cdot 4\text{H}_2\text{O}$ . *Yttrium methanesulphonate*,  $[\text{CH}_3(\text{SO}_2\cdot\text{O})]_3\text{Y}\cdot 2\frac{1}{2}\text{H}_2\text{O}$ . *Yttrium methanetriethylsulphonate*,  $[\text{CH}_3(\text{SO}_2\cdot\text{O})_3]_3\text{Y}\cdot 3\frac{1}{2}\text{H}_2\text{O}$ . *Yttrium ethanesulphonate*,  $(\text{EtSO}_2\cdot\text{O})_3\text{Y}\cdot 4\text{H}_2\text{O}$ . *Yttrium camphorsulphonate*,  $(\text{C}_{10}\text{H}_{17}\text{O}\cdot\text{SO}_2\cdot\text{O})_3\text{Y}\cdot 7\text{H}_2\text{O}$ . *Yttrium methoxysulphonate* [9] could not be obtained crystalline. The above salts are all very soluble.

*Yttrium salicylate*,  $(\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2)_3\text{Y}\cdot 3\frac{1}{2}\text{H}_2\text{O}$ , and *yttrium phthalate*,  $[\text{C}_6\text{H}_4(\text{CO}_2)_2]_3\text{Y}\cdot 3\text{H}_2\text{O}$ , were obtained by first preparing yttrium formate and then adding the required amount of the respective acids. These salts are both practically insoluble. *Yttrium phenylacetate*,  $(\text{CH}_2\text{Ph}\cdot\text{CO}_2)_3\text{Y}\cdot 3\text{H}_2\text{O}$ , and *yttrium glycolate*,  $[\text{CH}_2(\text{OH})\cdot\text{CO}_2]_3\text{Y}\cdot 2\text{H}_2\text{O}$ , were obtained as insoluble salts from the respective acids and yttrium hydroxide, whilst *yttrium phenoxyacetate*,  $(\text{Ph}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2)_3\text{Y}\cdot 3\frac{1}{2}\text{H}_2\text{O}$ , was prepared by precipitating a solution of yttrium chloride with phenoxyacetic acid, it being only slightly soluble in cold water.

The *phenoxyacetates* of samarium, neodymium, praseodymium, lanthanum, and cerium were prepared in the same manner as the yttrium salt, but they are much less soluble than the latter. They have the compositions  $\text{SmX}_3\cdot 3\frac{1}{2}\text{H}_2\text{O}$ ,  $\text{NdX}_3\cdot 2\frac{1}{2}\text{H}_2\text{O}$ ,  $\text{PrX}_3\cdot 1\frac{1}{2}\text{H}_2\text{O}$ ,  $\text{LaX}_3\cdot 2\frac{1}{2}\text{H}_2\text{O}$ , and  $\text{CeX}_3$ , where  $\text{X}=\text{Ph}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2$ .

Thorium is almost quantitatively precipitated from neutral solutions by the addition of excess of phenoxyacetic acid, a reaction which may be used for the separation of this element from the other rare earths, which are not thus precipitated. T. S. P.

**Europium.** CHARLES JAMES and J. E. ROBINSON (*J. Amer. Chem. Soc.*, 1911, 33, 1363—1365).—The materials worked up by the authors comprised: oxides from insoluble double sodium sulphates obtained from about 200 kilos. of yttrium minerals; all the samarium and gadolinium oxides derived from about 200 kilos. of Brazilian monazite; and about 110 kilos. of oxides obtained from the more soluble double potassium sulphates coming from very large amounts of Carolina monazite.

These crude oxides were converted into the double magnesium nitrates (compare Demarcay, *Abstr.*, 1901, ii, 511), which were recrystallised several times. When the mother liquors began to crystallise indefinitely, they were diluted and precipitated with oxalic acid. The oxalates so obtained were converted into oxides, and found to contain small quantities of lanthanum, cerium, and praseodymium, much neodymium and fair amounts of samarium, gadolinium, and yttrium earths. This material was again converted into the double magnesium nitrate, and recrystallised from 30% nitric acid. The neodymium, lanthanum, cerium, and praseodymium collected rapidly in the least soluble portion; the intermediate fractions consisted chiefly of the pale yellow samarium compound, while the most soluble portions were rich in gadolinium, and were coloured very pale pink by the yttrium metals. When crystals of the simple nitrates of the yttrium elements made their appearance, fractionation was proceeded with according to the bismuth magnesium nitrate method (Urbain and

Lacombe, Abstr., 1904, B. 349). By this means all samarium and europium were rapidly eliminated from the most soluble fractions. With regard to the yttrium earths, it was found that erbium and yttrium separated first, holmium next, and lastly dysprosium and terbium.

As soon as the fractions containing lanthanum, cerium, praseodymium, and neodymium had been freed from samarium, it was considered that all the europium had passed further along the series.

As the work proceeded, the europium band was seen to become stronger in the fractions between samarium and gadolinium, and when nearly all the samarium had been separated, bismuth was removed from the fractions containing europium by means of hydrogen sulphide, the fractions having been previously mixed according to their absorption spectra. The europium was then precipitated as oxalate, about 100 grams of this salt being obtained after two years' work. Some samarium was still present in the fractions nearest to that element, so the whole material was again fractionated with bismuth magnesium nitrate; when free from samarium, it was again converted into europium oxalate, which is to be further investigated.

About 5 kilos. of pure samarium oxalate and 4 kilos. of nearly pure gadolinium oxalate were also obtained.

T. S. P.

**The Action of Hydrogen Fluoride on Certain Oxides.** WALTER K. VAN HAAGEN and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1911, 33, 1504—1506).—The material to be tested was contained in a platinum boat placed in a platinum combustion tube, and hydrogen fluoride was then passed over it.

At a white heat aluminium oxide was quantitatively converted into the fluoride. Yttrium oxide at a red heat gave non-volatile fluoride or oxyfluoride. Lanthanum oxide was quantitatively converted into the non-volatile fluoride. Finely divided quartz was completely volatilised without the action of heat, whilst with titanium oxide a red heat was necessary.

Zirconium oxide and zircon mineral were completely converted into volatile fluoride at a red heat, as were also columbium and tantalum pentoxides. Tantalum fluoride is less volatile than columbium fluoride.

Cerium dioxide was changed quantitatively into non-volatile fluoride; tin stone gave a small quantity of a fluoride or oxyfluoride which was only volatile at a white heat, and thorium dioxide underwent a slight alteration only, without any volatilisation.

Columbium and tantalum were expelled from powdered columbite, and the metallic acids were completely volatilised from fergusonite. Potassium dichromate lost nearly all its chromic acid, whilst sodium tungstate was attacked with difficulty, and the tungstic acid not completely expelled. Phosphoric acid was expelled quantitatively from sodium pyrophosphate.

T. S. P.

**Metallographic Notes.** HENRI LE CHATELIER (*Rev. de Métallurgie*, 1911, 8, 367—376).—Several specimens of alloys prepared by Moissan in the electric furnace have been examined microscopically. Aluminium

carbide crystallises from aluminium in large plates, which disintegrate in air.

C. H. D.

**Constitution of the Alloys of Aluminium and Zinc.** WALTER ROSENTHAL and SYDNEY L. ARCHBUTT (*Phil. Trans.*, 1911, A, 211, 315—343; *Proc. Roy. Soc.*, 1911, A, 85, 389—392. Compare Shepherd, *Abstr.*, 1905, ii, 588).—Thermal and microscopic methods were employed in the investigation of the alloys. In the thermal experiments, cooling and heating curves were taken, large masses of alloy (300 grams) and slow rates of cooling being used. Further cooling curves were obtained with specimens of certain alloys which had been exposed to prolonged heating to allow of the completion of slow chemical changes. In the microscopic portion of the work specimens were examined which had been (a) slowly cooled from fusion; (b) annealed at certain definite temperatures and slowly cooled, and (c) annealed at certain temperatures and then quenched.

From the results obtained, an equilibrium diagram has been constructed which differs materially from that given by Shepherd. The liquidus and solidus curves are interpreted by reference to this diagram. Evidence has been obtained of the existence of a definite compound  $Al_2Zn_3$ , the micro-structure of which exhibits characteristic dendritic crystals which possess a marked habit of assuming six-rayed forms.

H. M. D.

**Solubility of Hydrogen in Copper, Iron, and Nickel.** ADOLF SIEVERTS (*Zeitsch. physikal. Chem.*, 1911, 77, 591—613).—The solubility of hydrogen in copper, iron, and nickel has been determined for pressures up to  $1\frac{1}{2}$  atmospheres and at intervals of temperature from  $400^\circ$  to  $1600^\circ$ . The solubility is independent of the extent of surface of the metal, so that the phenomenon is one of true solution and not of adsorption. At constant temperature the solubility in the solid and fused metals is proportional to the square root of the pressure, but below 100 mm. pressure the amount of hydrogen taken up diminishes rather more rapidly with the pressure than the above rule would indicate. At constant pressure the solubility increases with the temperature, and there is a sudden increase in solubility when the metal melts. The temperature-coefficient of the solubility is greater in fused than in solid copper. The change of  $\alpha$ - to  $\beta$ -iron is not recognisable on the solubility curve, but there is a rapid increase in solubility between  $850^\circ$  and  $900^\circ$ , connected with the transition from  $\beta$ - to  $\gamma$ -iron. All three metals give up hydrogen accompanied by "spitting" when they solidify in an atmosphere of the gas. At the respective melting points copper gives up 2 volumes, iron 7 volumes, and nickel 12 volumes of the gas.

At  $930^\circ$ , 100 grams of solid copper dissolve 0.108 mg.; at  $1420^\circ$  the fused metal takes up 1.097 mg. of hydrogen. At  $930^\circ$ , 100 grams of solid iron dissolve 0.431 mg.; at  $1550^\circ$  the fused metal takes up 8.5 mg. of hydrogen. At  $923^\circ$ , 100 grams of solid nickel dissolve 3.86 mg. of hydrogen. In each case the gas was corrected to 760 mm. pressure.

G. S.

**Passivity of Metals.** ERNST GRAVE (*Zellisch. physical. Chem.*, 1911, 77, 513—576).—There are serious objections to the oxide theory of passivity and to the suggestion that the passive and active metals have different valency. The only theory of passivity in accordance with the facts is that of Le Blanc (*Boltzmann Festschrift*, 1904, 183), who has pointed out that the solution pressure of iron in the passive state is much smaller than that in the active state. On this basis there are two possibilities: either pure iron is the active form and a negative catalyst is produced which renders it passive, or pure iron is the passive form and is rendered active by some positive catalyst which greatly increases its solution pressure. The author's results (described below) lend support to the latter view, the positive catalyst being  $H^+$  ions.

The ordinary impurities in iron and nickel have no effect on the passivity. Neither hydrogen peroxide nor ozone renders iron or nickel passive, although they render them less readily attacked, and the passive condition is retained longer in the presence of hydrogen peroxide. Further, the nature of the change from the passive to the active state is different from the fall of potential after polarisation by oxygen.

The main evidence in favour of the view that the activity of these metals is due to the presence of  $H^+$  ions is as follows. Iron and nickel become active when heated in hydrogen, but become passive when heated strongly in air, nitrogen or a vacuum. Molecular hydrogen, after being in contact with iron and nickel, does not alter the potential, but ionised hydrogen renders the metals active and ionised nitrogen renders them passive. Hydrogen ions are given off when a metal changes from the active to the passive state. When iron is saturated with  $H^+$  ions, the charge given off on heating is greatly increased. When iron is rendered active at one point by bringing it in contact with  $H^+$  ions, other parts of the metal are rendered active by diffusion.

G. S.

**A New Method for Determining the Extent of Rusting.** HUGO JACOB and R. КАЗЕВОНЕР (*Chem. Zeit.*, 1911, 35, 877—878).—The rusted article, which has been carefully weighed before rusting was allowed to take place, is made the cathode to an anode of platinum or carbon, preferably the former, in a suitable electrolyte. On the passage of a weak current, the gas which forms on the cathode detaches the rust from the surface, or else makes it so loose that it is easily brushed off. The article in question is thus very readily cleansed from all particles of rust, and after drying may be weighed to determine the extent of rusting. The best electrolyte is a 0.25–1% solution of sodium sulphate, and the current is so regulated that there is a vigorous evolution of gas from the electrodes. The time necessary for the cleansing process varies considerably, but the results obtained with this method are much more accurate than those got with the ordinary method of cleansing.

T. S. P.

**The Influence of Surface Condition on the Rusting of Iron.** KURT GRUND (*Metallurgie*, 1911, 8, 353—358).—Whilst cast

iron rusts uniformly over the surface, the rusting of wrought iron and mild steel is confined to local areas. The difference is due to the adherent character of the protective oxide film on cast iron, which is not readily dislodged by rust, whilst the film on wrought iron and steel readily scales off and allows the spongy rust to form. Alternations of wetness and dryness are better resisted by cast iron for the same reason.

C. H. D.

**The Rusting of Iron in Reinforced Concrete.** EDUARD DONATH (*Zeitsch. angew. Chem.*, 1911, 24, 1398—1402).—It is known that rusty iron or steel, embedded in concrete, gradually loses its rust. It is found that calcium hydrogen carbonate readily dissolves the ferrous hydroxide from rust, causing it to separate from the iron surface. The solvent action is accelerated by the presence of sulphates. Small quantities of pitrites and nitrates are formed in the action of lime on iron rust, the nitrogen being derived from ammonia contained in the rust. It has been suggested by Michaelis that the ferric oxide partly reacts with the lime of the concrete, forming a calcium ferrite. This is found to be the case. A mixture of iron rust with slaked lime is much more readily dissolved by dilute acetic acid or by alkaline sugar solution than the rust alone, and this reaction is probably, in part, the cause of the removal of rust by the concrete.

C. H. D.

**The Solubility of Carbon in Iron.** OTTO RUFF and OTTO GÖRCKE (*Metallurgie*, 1911, 8, 417—421. Compare Ruer and Iljin, this vol., i, 494).—Iron is melted in a graphite crucible, enclosed in a carbon tube resistance vacuum furnace. The temperature is read by means of a Wanner optical pyrometer. The iron is kept molten until saturated with carbon, and the crucible is then, by means of a special device, allowed to fall through the furnace into a closed vessel of ice-cold water. The quantity of dissolved carbon is estimated analytically. The experiments have been carried as far as 2620° without any separation into two layers.

The solubility of graphite in iron increases with the temperature from 1130°, the solubility curve having an abrupt change of direction at 1837° and 6.6% C, and a very distinct maximum at 2220° and 9.6% C. These two points correspond with the carbides  $\text{Fe}_3\text{C}$  and  $\text{Fe}_2\text{C}$  respectively. The rapidly quenched specimens show the structure of the metastable eutectic, with the excess of graphite in the form of plates parallel with the octahedral faces.

C. H. D.

**The Equilibrium Diagram of the Iron-Carbon Alloys.** OTTO RUFF (*Metallurgie*, 1911, 8, 456—464. Compare preceding abstract).—Although the freezing-point curve of the iron-carbon alloys has critical points corresponding with the carbides  $\text{Fe}_3\text{C}$  and  $\text{Fe}_2\text{C}$ , the equilibrium point  $3\text{Fe} + \text{C} \rightleftharpoons \text{Fe}_3\text{C}$  is always below the saturation point for the carbide, so that the only solid phase in contact with the solution is graphite. The carbides are endothermic compounds at temperatures above 700°. The diminished solubility of graphite in iron above 2220° is due to dissociation of the carbide  $\text{Fe}_2\text{C}$ . Below 2220° the reaction  $3\text{Fe}_2\text{C} = 2\text{Fe}_3\text{C} + \text{C}$  takes place, and at 1837° the reaction  $\text{Fe}_3\text{C} = 3\text{Fe} + \text{C}$ .



The boiling point of iron saturated with carbon is  $2750^{\circ}/10$  mm., whilst pure iron boils at about  $2220^{\circ}$  under the same conditions. The vapour of the alloys contains both iron and carbon.

In the process of solidification, the quantity of solid carbide formed is determined by its velocity of dissociation and the difference between its equilibrium concentration and its solubility, whilst the rate of cooling, by determining the extent of the supersaturation, also affects the result. Formulae are given for calculating the quantity of carbide formed under given conditions.

C. H. D.

**Influence of Thermal Treatment on the Properties and Structure of Hyperitectoid Steel.** A. JUNG (*Internat. Zeitsch. Metallographie*, 1911, 1, 209—255).—In steels containing from 1.0 to 1.5% of carbon, a martensitic structure gives the greatest hardness, and a pearlitic structure the greatest ductility, whilst troostite and sorbite give toughness. The limits of temperature between which the steel can be safely hardened by quenching become closer and also lower as the carbon is increased.

C. H. D.

**The Alloys of Iron and Antimony.** A. PORTEVIN (*Rev. de Metallurgie*, 1911, 8, 312—314).—The temperature at which pearlite is formed in alloys of iron and carbon is not appreciably altered by the presence of 1—9% of antimony. The antimony is retained in solid solution up to 6.5%; richer alloys show distinct crystals of an antimonide (compare Kurnakoff and Konstantinoff, *Abstr.*, 1908, ii, 391; Goerens and Ellingen; *Abstr.*, 1910, ii, 298).

C. H. D.

**The Structure of Galvanised Iron.** W. GUERTLER (*Internat. Zeitsch. Metallographie*, 1911, 1, 353—376).—Sections cut obliquely through the outer layers of galvanised iron show that the zinc and iron are separated by an intermediate layer of crystals of the compound  $\text{FeZn}_5$ . This compound is more electronegative than either iron or zinc, and thus accelerates corrosion if exposed. The zinc layer contains isolated crystals of the compound  $\text{FeZn}$ , which is also electronegative.

Zinc deposited from vapour by the dry process, or from solution by the electrolytic process, is porous, and also contains minute crystals.

C. H. D.

**The System  $\text{CrO}_3\text{--H}_2\text{O}$ .** ROBERT KREMANH [with J. DAIMER and E. BENNESCH] (*Monatsh.*, 1911, 32, 619—622).—The ice-curve of the system  $\text{CrO}_3\text{--H}_2\text{O}$  has been determined down to  $-74^{\circ}$ . It was not found possible to measure the eutectic temperature, but extrapolation of the ice curve and the solubility curve of chromium trioxide gives a eutectic point at  $-105^{\circ}$  and 57.2%  $\text{CrO}_3$ . Analysis of the crystals separating from more concentrated solutions shows that the only solid phase formed is the trioxide, no hydrate being found.

C. H. D.

**The Action of Acetic Anhydride on Uranium Nitrate.** ERWIG VÄRING (*Chem. Zeit.*, 1911, 35, 1005—1006).—When uranium nitrate (5 grams) is treated with an excess (20 c.c.) of acetic anhydride,

a solution is first formed, from which, after a short time, copious fumes of nitrogen peroxide are evolved. At the same time anhydrous uranyl acetate,  $\text{UO}_2\text{Ac}_2$ , is deposited as a yellow, crystalline powder. For the above reaction to take place in the cold, it is necessary that the acetic anhydride should contain a little acetic acid, or that another acid, for example, hydrochloric acid, be added to liberate some acetic acid from the uranium nitrate. If pure acetic anhydride is used, heat is necessary before the reaction commences.

If excess of the anhydride is not used, the only product obtained is a deep yellow liquid.

Thorium nitrate does not react as vigorously as uranium nitrate, and there is scarcely any action with lead or thallium nitrate.

Concentrated nitric acid reacts vigorously with excess of acetic anhydride in a short time, even in the cold.

T. S. P.

**Melting Point of Tantalum.** M. VON PIRANI and ALFRED R. MEYER (*Ber. deut. physikal. Ges.*, 1911, 13, 540—551).—An electrical method of measuring the melting point is described, which involves the use of an optical pyrometer. This method allows the determination to be made in a vacuum, and enables the metal to be completely isolated from other substances, which is a necessary condition because of the great reactivity of the metal at high temperatures. In these circumstances tantalum is found to melt at  $2850^\circ \pm 40^\circ$ .

H. M. D.

**The Atomic Weight of Tantalum.** WILLIAM H. CHAPIN and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1911, 33, 1497—1504).—The method used was the transformation of tantalum pentabromide into the oxide.

Tantalum oxide was obtained from recrystallised potassium tantalifluoride by treatment with sulphuric acid, subsequent hydrolysis, washing, and ignition. The pentabromide was prepared by conducting bromine vapours over a red-hot mixture of the oxide with sugar-carbon. To purify it, it was repeatedly sublimed in a vacuum, whereby very small quantities of a yellow residue were obtained, the analysis of which indicated the existence of a *tantalum oxybromide*,  $\text{TaOBr}_2$ . The pure pentabromide so obtained was then hydrolysed by water, and the acid and water evaporated off, the last traces of bromine being removed by evaporation with 10% nitric acid; the residue was then ignited to constant weight.

As a mean of eight experiments the atomic weight is found to be 181.80, the values varying from 181.68 to 181.91 ( $O = 16$ ).

T. S. P.

**Metallography of Selenium-Antimony Systems.** HENRI PÉLARDON (*Compt. rend.*, 1911, 153, 343—346).—Microscopic examination of selenium-antimony systems leads to the same conclusions as the previous study by the cryoscopic and electrical methods (this vol., ii, 575). Mixtures containing more selenium than the compound  $\text{Sb}_2\text{Se}_3$  show large crystals of this substance in a matrix of selenium. This is the only definite compound obtainable by fusion of the elements.

Mixtures containing 16—50% atomic proportions of selenium show two phases having almost the same density. The less dense contains the smaller amount of antimony and crystallises in long needles, whilst the other appears as irregular leaflets.

W. O. W.

### Mineralogical Chemistry.

**New Synthesis and New Occurrences of Covellite.** AUSTIN F. ROGERS (*School of Mines Quarterly, New York*, 1911, 32, 298—304).—Pseudomorphs of bluish-black covellite after zinc-blende from Big Coon mine, Galena, Kansas, gave analysis I; deducting unaltered zinc sulphide, this agrees with the covellite formula  $\text{CuS}$ . The covellite was no doubt produced by the action of copper sulphate solution on zinc-blende,  $\text{ZnS} + \text{CuSO}_4 = \text{CuS} + \text{ZnSO}_4$ . When finely-powdered zinc-blende was heated with copper sulphate solution in a sealed tube at 150—160° for some hours, the material became largely converted into bluish-black covellite (analysis II).

	Cu.	Zn.	Fe.	S.	$\text{SiO}_2$	Total.
I.	18.80	43.68	1.17	31.37	4.47	99.49
II.	60.10	5.98	0.74	32.75	—	100.75

Other occurrences of covellite are described from California, Colorado, Nevada, and Wyoming. The mineral occurs in the oxidised zone of ore-deposits, and is a product of decomposition of copper-pyrites, bornite, tetrahedrite, enargite, malachite, etc., and it also occurs as pseudomorphs after zinc-blende or galena.

L. J. S.

**Minerals from the Lead and Zinc District of Galena Joplin (Kansas-Missouri).** AUSTIN F. ROGERS (*Zeitsch. Kryst. Min.*, 1911, 49, 370—374; from *Univ. Geol. Survey, Kansas*, 1904, B, 445—509).—Descriptions are given of thirty-nine species collected in this mining district. Analyses are given of the following: Covellite pseudomorphous after zinc-blende (preceding abstract). I, Zinc-blende (wurtzite) from near Joplin: massive with botryoidal or stalactitic surface, of a dark brown colour, and under the microscope showing a granular structure and birefringence. In the cavities it contains small hemimorphic crystals of wurtzite. The results of the analysis are calculated to 100% after deducting  $\text{SiO}_2$  and  $\text{PbS}$ . II, Hydrozincite, white, opaque encrustation on smithsonite and hemimorphite, from Granby, Missouri; formula  $\text{ZnCO}_3 \cdot 2\text{Zn}(\text{OH})_2$ .

	Zn.	Fe.	S.	$\text{ZnO}$ .	$\text{CO}_2$ .	$\text{H}_2\text{O}$ .	$\text{SiO}_2$ .	Total.
I.	64.09	2.73	33.18	—	—	—	—	100.00
II.	—	—	—	72.80	14.94	12.12	0.14	100.00

L. J. S.

**The Constitution of Marcasite and Pyrites.** GEORGE W. PLUMMER (*J. Amer. Chem. Soc.*, 1911, 33, 1487—1492).—When marcasite or pyrites was heated at 250° with carbon tetrachloride in a sealed tube, the results indicated that about 75% of the iron in each mineral remained in the ferrous state. Sulphur monochloride was formed, however, and the results obtained are probably vitiated by the establishment of an equilibrium. With a 10% solution of cadmium sulphate instead of carbon tetrachloride, about 20% of the iron was found to be in the ferrous state. With arsenic trichloride instead of arsenic trisulphide, a colloidal solution of arsenic was obtained.

When either marcasite or pyrites is heated with excess of bismuth chloride at the fusion point of the latter and in an atmosphere of dry carbon dioxide, the mineral is completely decomposed within five minutes, and all the iron is found to be in the ferrous state. Only about 91% of the sulphur is in the form of bismuth sulphide, however, some of it being transformed into sulphur monochloride.

The authors draw the conclusion that in both marcasite and pyrites the iron is in the ferrous state, the formula being  $\text{Fe} < \frac{\text{S}}{\text{S}}$ .

T. S. P.

**Chemical Composition of a Telluride of Gold and Silver from Nagyag.** CARLO GASTALDI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1911, [iii], 17, 24—26).—Very different results have been obtained by different observers for the composition of krennerite, a rare telluride of silver and gold found in Transylvania and at Cripple Creek, Colorado. The author now shows that two different minerals have been known under this name, and proposes to retain the name krennerite for the compound,  $\text{AuTe}_2$ , occurring in rhombic crystals, whilst for the other mineral, of the formula  $(\text{Au,Ag})\text{Te}$ , the name *muthmannite* is suggested.

G. S.

**Chemical Composition of Goldschmidtite.** CARLO GASTALDI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1911, [iii], 17, 22—24).—A rare mineral obtained from Cripple Creek in Colorado has been shown by Hobbs (*Abstr.*, 1899, ii, 493) to contain gold, silver, and tellurium, and was termed by him goldschmidtite. Palache, on the other hand (*Abstr.*, 1901, ii, 109), regarded the new mineral as identical with sylvanite. The author now shows that goldschmidtite is a new mineral of the approximate composition  $(\text{Au,Ag})_2\text{Te}_3$ , whereas sylvanite has the formula  $(\text{Au,Ag})\text{Te}_2$ .

G. S.

**Neocolemanite, a Variety of Colemanite, and Howlite from California.** ARTHUR S. EAKLE (*Bull. Dep. Geol. Univ. California*, 1911, 6, 179—189).—A workable deposit of calcium borate, with seams 6—10 feet in thickness, occurs interbedded with black carbonaceous shales near Lang, Los Angeles Co., California. The material consists mainly of neocolemanite (anal. I), with embedded nodules of howlite (anal. II) and a little calcite. The neocolemanite is identical with colemanite in chemical composition, and in many of its physical

characters, but it shows slight differences in the angles of the monoclinic crystals ( $a:b:c=0.7771:1:0.5493$ ,  $\beta=111^{\circ}40'$ ), and in the optical properties (optic axial plane perpendicular to the plane of symmetry, as in colemanite, but  $c:\delta=-42^{\circ}30'$ ).

B <sub>2</sub> O <sub>3</sub>	CaO	SiO <sub>2</sub>	H <sub>2</sub> O	Total	Sp. gr.
I. 49.45	27.76	—	22.48	99.69	2.428
II. 45.56	28.26	14.81	11.37	100.38	2.581

L. J. S.

Barytes from the Freiberg Mining District. M. HENGLEIN (*Jahrb. Min.*, 1911, *Beil. Bd.*, 32, 71—100).—A crystallographic description of barytes from the mineral-veins of the Freiberg district. Brownish-yellow crystals from the Himmelsfürst mine contained only about 0.1% CaO; the colour is due to the presence of bitumen. Reddish platy barytes from the Kurprinz mine gave:

Ba	Ca	Fe	SO <sub>4</sub>	Total
58.17	0.28	0.57	41.04	100.06

L. J. S.

Synthesis of Smithsonite and Anglesite. GIUSEPPE PIOLTI (*Atti R. Accad. Sci. Torino*, 1911, 46, 783—788).—A rhombohedron of calcite was suspended by a platinum wire in 20% zinc sulphate solution contained in a closed vessel. After about seventeen and a-half years, the rhombohedron was found to be coated with needles of gypsum, and with a white mamillary incrustation which proved to be smithsonite. A solution of potassium nitrate left for about twenty years in contact with a fragment of zinc-blende was found to give the reactions for sulphates. The author, therefore, draws the conclusion that the formation of smithsonite in the superficial layers of the earth's crust (in calcareous rocks containing zinc-blende) is due to the oxidation of the blende to zinc sulphate, and the subsequent interaction of the latter with the calcium carbonate.

Similarly, a piece of galena left in potassium nitrate solution for seventeen and a-half years became covered with minute anglesite crystals, whilst the solution contained nitrite:  $4\text{KNO}_3 + \text{PbS} = \text{PbSO}_4 + 4\text{KNO}_2$  (compare Abstr., 1910, ii, 621).

T. H. P.

Mineralogical Notes [Cuprodesclowitzite, etc.]. F. N. GUILD (*Zeitsch. Kryst. Min.*, 1911, 49, 321—331).—Crystallographic descriptions are given of various minerals—vanadinite, wulfenite, linarite, caledonite, etc.—from Arizona and California. The following analyses (previously published in "The Mineralogy of Arizona" by the same author, 1910) are given: I, Cuprodesclowitzite, occurring as a black crystallised crust, 1—2 mm. thick, on large crystals of vanadinite, from the Old Yuma mine, near Tucson, Arizona; the colour of the powdered mineral is pale olive-green. II, Desclowitzite, occurring as small, black crystals with yellowish-green streak, from Argentina. Both analyses agree with the usual formula,



PbO	CuO	FeO	ZnO	MnO	V <sub>2</sub> O <sub>5</sub>	As <sub>2</sub> O <sub>3</sub>	Cl	H <sub>2</sub> O	Insol.	Total
I. 52.26	14.64	—	6.71	—	23.02	—	—	2.52	—	98.31
II. 52.26	12.1	0.56	13.15	0.56	23.05	0.11	0.08	2.27	0.78	99.13

L. J. S.

**Ferritungstite, a New Mineral.** WALDEMAR T. SCHALLER (*Amer. J. Sci.*, 1911, [iv], 32, 161—162).—The sample of tungstic-ochre described is from the Germania tungsten mine, Deer Trail mining district in the north-eastern part of the State of Washington, where it occurs as an alteration product of wolframite in massive quartz. It is a pale yellow or brownish-yellow ochre, but under the microscope is seen to consist of minute, hexagonal plates, which are optically isotropic on the base. Analyses of small quantities of material gave:

WO <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Ignition (H <sub>2</sub> O)	Insol. (Quartz)	Total
87.1	26.6	18.6	14.7	97.0
85.8	27.3	20.9	[16.0]	100.0

These results agree with the formula Fe<sub>2</sub>O<sub>3</sub>.WO<sub>3</sub>.6H<sub>2</sub>O. The mineral thus differs from ordinary tungstic-ochre, or tungstite, and it is named ferritungstite.

L. J. S.

**Some Presumed Chemical Effects of Pressure in Mineral Metamorphism.** GIORGIO SPEZIA (*Atti R. Accad. Sci. Torino*, 1911, 46, 682—698).—The author has submitted to experimental examination the statements of van Hise (*Treatise on Metamorphism, Monographs U.S. Geol. Survey*, 1904, 47) on the effect of pressure in causing chemical change. This writer supposes that under the influence of high pressure (1) silicates are formed from silicon dioxide and carbonates; (2) combined water may be squeezed out of hydrated minerals; (3) combined oxygen may be removed in the same way. In regard to the first statement it has been shown that hydrated silicon dioxide and calcium carbonate do not react under a pressure of 6000 atmospheres for one year (*Atti. R. Acad. Sci. Torino*, 1905, 40, 698). The author has subjected samples of limonite, alum, and alabaster to a pressure of 8000 atmospheres for eight months at 15—24° without effecting any dehydration. Crystals of gëthite maintained under a pressure of 9500 atmospheres for twenty-six days at 15° showed no loss of water, although crystals of the substance were almost dehydrated after having remained in water in an autoclave for seven days at 320—330° (corresponding with a pressure of 135 atmospheres). It has also been impossible to obtain evidence of the occurrence of deoxidation at high pressures. When a mixture of cupric oxide and potassium (or magnesium) was kept under a pressure of 9500 atmospheres at 18° for thirty days, no oxidation of the metal occurred, although pressure might be expected to favour the reaction, because it would be attended by a diminution of the molecular volume.

Calcite (D 2.73) and aragonite (D 2.92) when kept under a pressure of 7000 atmospheres at 15—25° for six months both remain unchanged, so that van Hise's statement that high pressure favours the production of the densest form of minerals lacks confirmation.

R. V. S.

## Physiological Chemistry.

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**The Chemical Regulation of Vascular Tone as Studied on the Perfused Blood-vessels of the Frog.** DONALD R. HOOKER (*Amer. J. Physiol.*, 1911, 28, 361—367).—Vascular tone is increased by calcium ions and oxygen, and decreased by sodium and potassium ions, carbon dioxide, and urea. The musculatures of the vascular system and of the intestine give opposite results under the influence of carbon dioxide and oxygen. W. D. H.

**The Behaviour of Acetone Substances in Intermediary Metabolism.** H. CHR. GEELMUYDEN (*Zeitsch. physiol. Chem.*, 1911, 73, 176—191).—Acetoacetic acid and  $\beta$ -hydroxybutyric acid administered to phloridzinised rabbits on a constant cabbage diet produced in all cases a decided increase in the sugar excreted in the urine. It is considered that these "acetone-substances" are first synthesised into glycogen in the liver. W. D. H.

**Mucic Acid and Intermediary Carbohydrate Metabolism.** WILLIAM C. ROSE (*J. Biol. Chem.*, 1911, 10, 123—138).—Mucic acid in large doses is only, in part, excreted in the urine; a very small increase occurs in the oxalic acid of the urine, and so mucic acid is hardly a precursor of oxalic acid. Large doses of galactose and lactose do not lead to mucic acid in the urine. Mucic acid is therefore not an intermediary product in the metabolism of galactose-yielding sugars. The experiments were made on dogs and rabbits. W. D. H.

**Protein Metabolism. II.** FRANZ FRANK and ALFRED SCHITTENHELM (*Zeitsch. physiol. Chem.*, 1911, 73, 157—175).—Two dogs were fed on a diet containing the necessary amount of fat and carbohydrate; nitrogen was supplied in the form of dog's flesh, ox flesh, and other forms of meat in the dried state, as well as in casein, blood albumin, peptone, and the abietic products of complete digestion of fish, beef, egg albumin, and milk. Each article mentioned was employed alone for periods of from seven to twenty-six days. Two results of importance stand out: (1) nitrogenous metabolism was practically the same whatever form of protein food was given; dog's flesh for the dog has no special value; (2) the abietic products maintained metabolism as well as the undigested protein. W. D. H.

**Velocity of Decomposition of Food-protein and Body-protein.** HEINRICH VON HORSSLIN and E. J. LESSER (*Zeitsch. physiol. Chem.*, 1911, 73, 346—364).—The relative value of protein from dog's and ox flesh in feeding dogs after inanition has been pointed out by Michaud. The present observations, although they show small differences, are in favour of Michaud's view that an animal utilises best protein obtained from another animal of the same kind, do not prove that the advantage is a great one. W. D. H.

**Formation of Proline in the Digestion of Gliadin.** EMIL FISCHER and E. S. LONDON (*Zeitsch. physiol. Chem.*, 1911, 73, 398—400).—In the dry residue of the chyme obtained from about the middle of the intestine by a fistula in a dog fed on gliadin, the amount of free proline found was approximately that obtained by Abderhalden and Samuely after complete hydrolysis by acids. W. D. H.

**A Mode of Resorption of Reserve Fat.** MAURICE PIETTRE (*Compt. rend.*, 1911, 153, 487—490).—The fat of sheep suffering from distomatosis, in which the liver has become invaded by the embryos of *Fasciola hepatica*, undergoes a change in appearance and acquires a peculiar farinaceous consistence. Determination of the iodine number and other constants shows that no chemical change has taken place. The subject has been investigated histologically. W. O. W.

**Histo-chemistry of Spermatozoa.** II. HERMANN STEUDEL (*Zeitsch. physiol. Chem.*, 1911, 73, 471—477. Compare this vol., ii, 626).—The heads of herring spermatozoa washed with water and freed from fat by alcohol and ether should theoretically yield 71·8% nucleic acid and 28·2% protamine. By phosphorus estimation, supposing all the phosphorus to be in the form of nucleic acid, only 65·4% of nucleic acid is present. By extraction with 1% sulphuric acid, the loss of protamine is even greater, 19·78 instead of 28·2%. By estimating the yield of arginine, there is still a loss of the protamine reckoned therefrom of 5·9%. Evidence is adduced that the spermatozoa heads contain a small quantity of a protein which gives Millon's reaction. W. D. H.

**The Relation between the Physical, Chemical, and Electrical Properties of Nerves.** V. The Action of Cinchonamine Hydrochloride on Frog's Nerves. F. O'B. ELLISON (*J. Physiol.*, 1911, 43, 28—33).—Cinchonamine hydrochloride increases the injury current, and abolishes the action current of a nerve. It does not abolish excitability or conductivity. W. D. H.

**The Oxidation of Isolated Animal Tissues.** ARTHUR HARDEN and HUGH MACLEAN (*J. Physiol.*, 1911, 43, 34—45).—An apparatus for estimating the post-mortem gaseous metabolism of minced organs is described and figured. Such organs have no more power of producing carbon dioxide from sugar in an atmosphere of oxygen than they have in one of nitrogen or hydrogen. Tissue juices prepared by the aid of kieselguhr and aqueous or saline extracts of tissues possess little or no respiratory activity. Oxidation in minced tissue is markedly lowered by grinding with sand, mixing with kieselguhr, or by the use of antiseptics. The figures obtained throughout are considerably lower than those given by Battelli and Stern. W. D. H.

**The Indophenol Oxydase of Mammalian and Avian Tissues.** HORACE M. VERNON (*J. Physiol.*, 1911, 43, 96—108).—In twelve mammals, the heart muscle is richest in this oxydase, and with



the exception of the hedgehog, the liver is the poorest. The harvest mouse has more than the common mouse, and that more than the rat, but the amount in each tissue in the larger mammals from the guinea-pig upwards is nearly constant. These results roughly correspond with the degree of oxygen saturation as determined by Ehrlich. In birds the oxydasic power of the tissues and the respiratory exchange run parallel. The oxydasic power depends largely on the power a tissue possesses of sustained activity. Cold-blooded animals have very little oxydase, and the same is true for embryonic tissues, the liver excepted.

W. D. H.

**The Composition of the Heart of Man and Dog.** RICHARD LEDERER and KARL STOLTZ (*Biochem. Zeitsch.*, 1911, 35, 108—112).—The following estimations were made: Water content, amount of substance extractable by ether, glycogen, potassium + sodium chlorides, sodium, potassium, chlorine, phosphorus, sulphur, nitrogen, and total ash. No appreciable difference could be detected between normal hearts and hearts pathologically affected. Dogs' hearts contain less sodium, chlorine, and sulphur than the human heart, whereas the phosphorus and nitrogen content is higher. The results are tabulated.

S. B. S.

**Action of Various Salts on Isolated Muscle.** I. Sodium, Potassium, and Ammonium Salts. P. G. WARD (*Proc. physiol. Soc.*, 1911; *J. Physiol.*, 43).—The abolition of response to direct excitation in the frog's sartorius is most readily produced by potassium salts; ammonium and sodium salts follow in the order named. The recovery in saline solution is rapid in the case of potassium salts, and that from the other salts is much less pronounced.

W. D. H.

**The Formation of Glycine in the Animal Body.** I. The Synthesis of Hippuric Acid in the Liver of the Rabbit. ERNST FRIEDMANN and HERMANN TACHAN (*Biochem. Zeitsch.*, 1911, 35, 88—103).—It has been shown that in the excretion of hippuric acid more glycine can be removed from the body than is ingested, and, furthermore, that young animals can have combined in their proteins more glycine than is contained in the ingested proteins. Investigations were therefore undertaken with the view of throwing light on the method of synthesis of glycine in the animal body. For this purpose, the formation in the rabbit's liver was studied, the method of experiment adopted being the perfusion of this organ in Friedmann's apparatus with defibrinated rabbit's blood to which benzoic acid had been added, and the estimation of the hippuric acid formed under various conditions. From a large series of experiments, it was found that the hippuric acid quantities formed varied greatly in different livers, but that the addition of glycine or its homologues, or of the lower fatty acids (as sodium salt), did not increase the amount. It was concluded therefore that glycine is directly formed in the liver when the latter is perfused with blood containing benzoic acid.

S. B. S.

**Uric Acid Formation.** VII. (1) Failure of Regeneration of Uric Acid in Hunger. (2) Destruction and Formation of Uric Acid in Birds. (3) Uric Acid Synthesis in Mammals and Birds. GUIDO IZAR (*Zeitsch. physiol. Chem.*, 1911, 73, 317—334).—The livers of dogs in a state of inanition have only a feeble uricolytic power, and they do not produce regeneration of the uric acid on the addition of the blood of fasting animals. A considerable amount of uric acid is, however, formed if the blood of a well-fed animal is used. The bird's liver freed from blood has the power of decomposing uric acid. Livers of birds killed two hours after feeding are able to re-form (in the absence of oxygen) the uric acid which has disappeared; in the latter phenomenon, an enzyme (thermolabile) in the blood, and a co-enzyme (thermostable) in the liver are concerned; the co-enzyme is soluble in alcohol and is not present in the kidneys. Uric acid synthesis from dialuric acid and urea occurs, not only *in vitro*, but in artificial perfusion of the liver in both mammals and birds. The addition of lactic, sarcosolactic, tartaric, acrylic, oxalic, and mesoxalic acids leads in the absence of oxygen to no formation of uric acid. Among the substances which are uric acid formers in birds, only ammonium carbonate and urea in the presence of carbon dioxide lead to an increase of uric acid.

W. D. H.

**Probable Formation of Adrenaline in the Animal Body.** CASIMIR FUNK (*Proc. physiol. Soc.*, 1911, iv.; *J. Physiol.*, 43).—3:4-Dihydroxyphenylalanine (*Trans.*, 1911, 99, 554) has no action on blood-pressure, and is not toxic; when incubated with suprarenal glands, or with a mixture of these glands with liver and pancreas, no adrenaline is formed. It is, however, still possible that the first stage of adrenaline formation may occur in the intestine, and may be of a similar nature to the transformation in the intestine of tyrosine into *p*-hydroxyphenylethylamine.

W. D. H.

**Calcium Resorption and Calcification.** MASAHIKO TANAKA (*Biochem. Zeitsch.*, 1911, 35, 113—133).—The solvent effect of liquids (water, 0.9% sodium chloride solution, or ox-serum) saturated with carbon dioxide on bone and allied material, such as teeth and ivory, was studied, and the rate of solution per day per 100 sq. mm. noted. In all cases the solution was found to be quite appreciable. The solvent action of the tissues was also studied by embedding weighed pieces of ivory in the various tissues of living animals and estimating the rate of absorption by weighing. This was found to vary from 0.00070 (in the kidneys) to 0.00118 gram (in the spleen) per sq. mm. per day. The formation of calcium deposits in the living organism after injection of calcium salts was also studied. It was found that in rabbits, dogs, guinea-pigs, and mice, deposits were formed after injection both of soluble and insoluble calcium salts, the formation commencing after two days when the injected dose was not too small. The deposits do not form at the point of injection, but in the neighbouring tissues. Attempts to produce calcium metastases, such as met with pathologically, were not successful under the varying conditions of experiment tried (including simultaneous injection of

phosphates). Analyses of calcium deposits formed after introduction of carbonates and phosphates were made. From the results the conclusion is drawn that the constancy of the composition of calcium deposits and of bone is not due to the existence of a definite chemical compound, but to the practically constant proportions of carbonates and phosphates in the blood-plasma and lymph. The results confirm the conclusions arrived at by Wells and Benson. S. B. S.

**Melanin. II. The Pigmentation of the Adult Periodical Cicada (*Tibicen septendecim*).** ROSS A. GORTNER (*J. Biol. Chem.*, 1911, 10, 89—94).—The "seventeen year" locust pupa spends seventeen years in subterranean regions, and on emerging from the ground is fully matured in from twenty to sixty minutes. At first it is white, and then in a few hours develops black and orange patches; it then becomes deep black, except the eyes, which are red, and the wing veins, which are orange. This is due to the interaction of a chromogen and an oxydase of the tyrosinase group; the latter is secreted with the new cuticle; it is soluble in water, and rendered inactive by alcohol and by prolonged dialysis in collodion bags. W. D. H.

**Melanin III. The Inhibitory Action of Certain Phenolic Substances on Tyrosinase. A Suggestion as to the Cause of Dominant and Recessive Whites.** ROSS A. GORTNER (*J. Biol. Chem.*, 1911, 10, 113—122).—If albinos are crossed with a coloured variety, the first generation are all coloured. Other forms of white animals differ from the true albino in giving white offspring. In the former case, the white is a recessive, in the latter a dominant, characteristic to adopt Mendelian nomenclature. The difference must ultimately be due to the interaction of chromogens and oxydases in the skin. Aromatic compounds with two hydroxyls in the meta-position inhibit the action of tyrosinase on tyrosine and other chromogens. If tyrosine is converted in the body into either 3-hydroxy- $\alpha$ -anilinopropionic acid (that is, the hydroxyl is shifted from 4 to 3), or if an additional hydroxyl is added ortho to the alkyl chain, a compound is secured which would be incapable of pigment formation under the influence of tyrosinase, and would inhibit pigment formation even if tyrosine and tyrosinase were both present. Such a condition would produce dominant whites. Albino whites lack either the enzyme, the chromogen, or the inhibiting factor. W. D. H.

**Composition of the Secretion of *Timarcha tenebricosa*.** E. WACE CARLIER and C. LOVATT EVANS (*Premier Congrès International d'Entomol. Brussels*, 1910).—The red secretion of the bloody-nosed beetle issues from between the jaws. The ash contains calcium, iron, magnesium, potassium and sodium, phosphoric acid, and chlorine. The most abundant salt is calcium phosphate. The secretion contains albumin and globulin, the pigment is mainly lipochrome, and is soluble in alcohol and ether. The fluid bubbles with sodium hypobromite, and contains a copper-reducing substance in small quantities. No enzymes were found. No quantitative analysis was made owing to the paucity of material. W. D. H.

**Some Energy Factors of the Urine Excreted After Severe Muscular Exercise.** HAROLD L. HIGGINS and FRANCIS G. BENEDICT (*Amer. J. Physiol.*, 1911, 23, 291—300).—Urea and ammonia (C:N ratio 0.43 and 0 respectively) tend to keep this ratio in the urine low; uric acid, creatinine, and other carbonaceous compounds raise this ratio. The value of a study of the C:N and calorie:N ratios in the urine is very great in nutrition experiments and in pathology. The ratios (methods for determining which are given) were estimated in eighteen urines after a long-distance running race. In twelve cases the values were normal; the remaining six gave high ratios, probably due to perverted protein metabolism. In view of the fact that the calorie:carbon ratio is constant, the advantage is pointed out of the development of either a volumetric method or a wet process by which estimations of carbon in urine can be rapidly and accurately made.

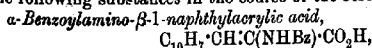
W. D. H.

**Differences in the Urine of Health and Carcinoma.** KENJI KORO (*Zeitsch. physiol. Chem.*, 1911, 73, 416—433).—The amount of nitrogen which is precipitable by metallic salts (zinc and barium) is about twice as great in the urine of carcinoma as in health. The disturbance of metabolism to which this is attributable is unknown; nor is it known if it is characteristic of cancer.

W. D. H.

**The Degradation of the Naphthalene Ring in the Animal Body.** T. KIKKOJI (*Biochem. Zeitsch.*, 1911, 35, 57—87).—After ingestion of  $\beta$ -1-naphthylalanine by a dog, a nitrogenous substance was excreted in the urine, of which the composition has not yet been definitely determined. After ingestion of the corresponding  $\beta$ -2-compound a similar substance was also excreted (with the probable formula  $C_{15}H_{16}O_2N_2$ ), but in relatively smaller quantities. In addition, 3-naphthylacetic acid and somewhat larger quantities of hippuric acid were excreted. After ingestion of  $\beta$ -naphthylpyruvic acid,  $\beta$ -naphthylacetic and hippuric acids were also excreted. A nitrogen derivative was not in this case isolated. These results indicate the influence of the position of the side-chain on the degradation of the naphthalene ring in the animal body, which is discussed theoretically in some detail by the author, and compared with the various known degradations of the benzene ring, such as is found both in alcaptonuria and in normal cases.

The naphthylalanines were prepared by condensing the naphthaldehydes with hippuric acid to the lactimides of the  $\alpha$ -benzoylamino-naphthylacrylic acids. The benzoylamino-naphthylacrylic acids were obtained from this by hydrolysis with potassium hydroxide were reduced by sodium amalgam to benzoylnaphthylalanines, from which, by scission of the benzoyl group with acid, the naphthylalanines were obtained in the form of the hydrochlorides. The author gives improved methods for preparing the naphthaldehydes, and obtained the following substances in the course of the research:



yellow needles, m. p. 221°; the *lactimide*,  $C_{16}H_{13}ON$ , reddish-yellow needles, m. p. 168—169°;  $\beta$ -1-Naphthylalanine,



colourless leaflets, m. p. 240° (decomp.); the *hydrochloride* forms colourless needles, and the *benzoyl* derivative consists of colourless, glistening leaflets, m. p. 192—193°.

$\alpha$ -Benzoylamino- $\beta$ -2-naphthylacrylic acid, pale yellow, stout needles, m. p. 229—230° (decomp.); the *lactimide*, yellow needles, m. p. 147—148°;  $\beta$ -2-Naphthylalanine, radiating spheres, m. p. 263—264° (decomp.); the *hydrochloride* was not obtained pure; the *benzoyl* derivative forms glistening leaflets, m. p. 164°.

$\beta$ -Naphthylpyruvic acid,  $C_{16}H_{13} \cdot CH \cdot CO \cdot CO_2H$ , prepared from  $\alpha$ -benzoylamino- $\beta$ -2-naphthylacrylic acid by boiling with potassium hydroxide solution, crystallises in colourless, wide needles and irregular leaflets, m. p. 192° (decomp.). S. B. S.

### The Degradation of Carboxylic Acids in the Animal Body.

XIII. The Behaviour of Furylacrylic and Furoylacetic Acids in the Animal Body. ERNST FRIEDMANN (*Biochem. Zeitsch.*, 1911, 35, 40—48. Compare Abstr., 1910, ii, 977).—Furylacrylic acid after subcutaneous injection into the body of the dog is excreted unchanged to the extent of 29%; in addition, pyromucic acid (22.4%) is excreted and furyl methyl ketone. The results might indicate that furoylacetic acid is formed as an intermediate product, although direct evidence of its formation was wanting. When, however, this substance was injected, either as an ester or sodium salt, neither pyromucic nor pyromucuric acids could be detected. It is therefore concluded that a  $\beta$ -keto-acid is not formed as an intermediate stage in the degradation of furylacrylic or furylpropionic acids, thus confirming an opinion formerly expressed by the author that  $\alpha\beta$ -unsaturated acids can be degraded to acids with two less carbon atoms without the intermediate formation of keto-acids. S. B. S.

### The Degradation of Carboxylic Acids in the Animal Body.

XIV. The Removal of Hydrogen in the Animal Body. ERNST FRIEDMANN (*Biochem. Zeitsch.*, 1911, 35, 49—56).—In view of the various observations on the formation of unsaturated acids from saturated in the animal body, and to throw light on the processes involved in the removal of hydrogen, the author tried the effect of feeding dogs with the following hydrogen-rich substances: cyclohexanecarboxylic acid, hexahydroanthranilic acid, cyclohexanecarboxylic acid, and cyclohexanecarboxylic acid. The two former only caused a notable increase in the amount of hippuric acid excreted. A method for isolating this substance from the urine is described. S. B. S.

Carbohydrate Metabolism. I. The Influence of Hydrazine on the Organism with Special Reference to the Blood Sugar Content. FRANK P. UNDERHILL (*J. Biol. Chem.*, 1911, 10, 159—168).—Hydrazine sulphate subcutaneously injected in dogs and rabbits in doses of 0.2 gram per kilo. of body-weight causes death. Half this quantity is usually followed by recovery, and lowers the amount of

sugar in the blood of dogs; this effect is not constant in rabbits. During a short period of inanition, assimilation of dextrose after hypodermic administration is as good as in normal well-fed dogs. Dextrose in subcutaneous doses of 5 grams per kilo. promptly causes death if the dogs had previously been treated with non-fatal doses of hydrastine. Hydrazine introduced into the blood stream causes no appreciable immediate influence on arterial blood-pressure.

W. D. H.

**Action of an Oxazine (3:5:9-Triaminophenoxazonium Chloride) on Trypanosomes.** A. LAVERAN and ROUDSKY (*Compt. rend.*, 1911, 153, 226—230. Compare Kehrman and Sager, *Abstr.*, 1903, i, 279).—The experiments were conducted on mice by intramuscular injection, using a 0.1% aqueous solution of the substance. Both *in vivo* and *in vitro* the centrosomes show a marked affinity for the dye, which also brings about morphological changes. In *T. Brucei* the centrosomes disappear, and the new modification is transmissible by heredity. Other species of trypanosomes show the same behaviour in variable degrees; in general, their virulence is diminished, but often only temporarily.

W. O. W.

**The Physiological Effects of Alkaloids of *Zygadenus Intermedius*.** PHILIP H. MITCHELL and GEORGE SMITH (*Amer. J. Physiol.*, 1911, 23, 318—329).—An alkaloidal preparation from *Zygadenus intermedius* (one of the death camas, which is so destructive to sheep) causes slowing of the heart by acting on the cardio-inhibitory centre, slowing of the respiration by acting on the respiratory centre, vasodilatation, purgation, and emesis. In quantities approaching the fatal dose (5 mg. per kilo. of guinea-pig) the heart is rapid and irregular, and the respiration convulsive. In fatal doses the heart stops before respiration.

W. D. H.

**Pharmacology of Substances Behaving Like Digitalis.** ALBERTUS SLUYTERMAN (*Zeitsch. Biol.*, 1911, 57, 112—134).—The action of antiarin, helleborein, oleandrin, infusion of *Folia Digitalis*, barium chloride, and methyl-violet on the ventricle of the frog's heart was examined. The general effect of all is the same, so that the author classes them as digitalis substances. Examination of the curves, however, reveals certain differences; a scale of activity for different dilutions can be drawn up for antiarin, digitalis infusion, and barium chloride, but not for the others.

E. J. R.

***p*-Iodophenylarsinic Acid and Some of its Derivatives. II. Pharmacological Action.** EFISIO MAMELI and ALDO PATTA (*Arch. Farm. speriment. Sci.*, 1911, 11, 475—484. Compare *Abstr.*, 1909, 543; 1910, i, 531).—From experiments with guinea-pigs, rabbits, and dogs, the authors find that *p*-iodophenylarsinic acid is much more toxic than atoxyl, so that the displacement of  $\text{NH}_2$  by iodine increases toxicity. The absorption of the substance requires considerable time: iodine does not appear in the urine until three to five hours after administration of the drug. The absorption of the iodide of the acid

is even slower. After administration of the acid, all the iodine of the urine is in organic combination, but the iodide yields also ionic iodine in the urine. In both cases arsenic is present in inorganic combination, and the appearances found in the animals coincide with those of arsenic poisoning.

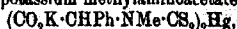
R. V. S.

#### *p*-Iodophenylarsinic Acid and Some of its Derivatives.

III. Action on Metabolism, on the Circulation, and on Trypanosomes. ERISIO MAMMI and ALDO PATTA (*Arch. Farm. speriment. Sci.*, 1911, 12, 1—7. Compare preceding abstract).—In rabbits, *p*-iodophenylarsinic acid appears to diminish the rate of the metabolism of the albumins. The substance does not affect the pulse or the arterial pressure. Neither the acid nor its iodide has any action on *Trypanosoma Brucei*.

R. V. S.

Mercurial Therapeutics of Experimental Syphilis in the Rabbit and of Brazilian Spirochælosis. L. LAUNOY and G. LEVADITI (*Compt. rend.*, 1911, 153, 304—306).—The mercury derivative of the dithiocarbamate of potassium methylaminoacetate,



(Fourneau; this vol., i, 623), has a distinct curative action in syphilis of rabbits and spirochælosis of fowls when administered by intravenous injection. Instances of complete cure are recorded.

W. O. W.

Action of Senecio Alkaloids and the Causation of Hepatic Cirrhosis in Cattle. ARTHUR R. CUSHNY (*Proc. Roy. Soc.*, 1911, B, 84, 188—190).—Whilst the various species of Senecio in this country are usually considered harmless, in Canada and New Zealand the species *Senecio Jacobaea*, apparently identical with the common ragwort, is associated with hepatic cirrhosis in cattle, and in S. Africa this disease is associated with *Senecio Burchellii* and *S. latifolius*, from which Watt (*Trans.*, 1909, 95, 466) obtained two alkaloids, senecifoline and senecifolidine.

The results of experiments with these two alkaloids showed that they are equally toxic and produce the same symptoms. Very large amounts have an effect on the central nervous system resembling that seen in many convulsive poisons, whilst with smaller quantities the chief effect is hæmorrhage, which may occur in almost any organ and is constant in the liver and nearly always present in the stomach and bowels.

Experiments with extract of English ragwort and of *S. silvestris* collected in Yorkshire gave negative results. *S. vulgaris* (common groundsel) collected in England proved poisonous, the animals dying from symptoms resembling those produced by senecifoline, but with diarrhoea.

N. H. J. M.

#### The Combination of Tetanus Toxin [with other Substances].

II. SIEGFRIED LOEWZ (*Biochem. Zeitsch.*, 1911, 34, 495—511. Compare this vol., ii, 638).—The tetanus toxin, in varying concentrations, was shaken with brain substance, and the coefficient of distribution between the two phases ascertained by determining the number of

minimal amount in the aqueous phase at the end of the experiment. The results indicate that there can be no question of a chemical combination between the brain substance and the toxin; they indicate rather a distribution of the latter between the two phases in the sense of Henry's law.

S. B. S.

**The Action of Crotalus Poison.** IVAR BANG and E. OVERTON (*Biochem. Zeitsch.*, 1911, 34, 428—461).—A solution of the dried crotalus poison in pure water acts toxically on tadpoles only when the solution reaches a concentration of 1%. By the addition, however, of small quantities of hemolysed blood-corpuscles, the toxicity is increased three hundred-fold, and is then about one-third of that of cobra poison. Within certain limits the toxicity of the crotalus poison increases with increasing quantity of blood-corpuscles, an addition of less than 0.1 c.c. to 25 c.c. of the toxin solution exerting no action, whereas 1 c.c. exerts the maximal action. This is probably due to the action of the phosphatides, Merck's "lecithin" exerting a similar action. The toxic action of crotalus is diminished by momentarily boiling the solution. A solution of the poison in blood serum is four to five times stronger than the corresponding solution in water. The serum must be rendered innocuous to the tadpoles by previously heating it to 50°. The crotalus poison differs from the cobra poison, in that in concentrations sufficient to paralyse the central nervous system it also causes stoppage of the circulation. The solution in water (but not in serum) injures the skin epithelium. In consequence of these two last actions, the toxic action, unlike that of cobra poison, is not reversible when the tadpoles are transformed to a toxin-free medium. The addition of calcium chloride to a crotalus toxin solution activated by blood-corpuscles diminishes or destroys the toxicity. The antivenin preparation (from the Pasteur Institute of Lille) as strongly diminishes the toxic action as it does that of cobra poison. The toxic action from the crotalus bite appears to come into play when the secretion of the poison glands exerts its action on the blood-corpuscles.

S. B. S.

## Chemistry of Vegetable Physiology and Agriculture.

**Electrical Effects Accompanying the Decomposition of Organic Compounds.** M. C. POTTER (*Proc. Roy. Soc.*, 1911, B, 84, 260—275).—Experiments performed with yeast and dextrose, invertase, diastase, and *B. coli communis* all show that the disintegration of organic compounds by micro-organisms is accompanied by the liberation of electrical energy. The electrical effects express the activity of the micro-organisms, and are influenced by the factors temperature, concentration of the nutrient, and the number of organisms present. They take place only within the ordinary temperature limits of biological activity.



A special type of galvanic cell with platinum electrodes is described. The charge was found to correspond with an E.M.F. of 0.3 to 0.5 volt between the fermenting and non-fermenting fluids. E. F. A.

**The Significance of Dihydroxyacetone as an Intermediate Product of Alcoholic Fermentation.** S. KRAUSCHANOFF (*Ber. Deutsch. bot. Ges.*, 1911, 20, 322-327).—Jensen states that dihydroxyacetone is fermentable by yeast, and argues that it is an intermediate product in the fermentation of sugar. The author does not consider that Jensen's methods were sufficiently refined; the small amounts of carbon dioxide supposed to arise from fermentation may in reality have come from the animal charcoal. E. J. R.

**Alteration in the Fermentative Properties of Yeast Cells on Killing by means of Acetone.** REINHOLD O. HERZOG and O. SALADIN (*Zeitsch. physiol. Chem.*, 1911, 73, 263-283).—A comparison is made of the relative velocities of fermentation of dextrose, levulose, mannose, and galactose by living yeast and by the same yeast after killing with acetone. Action was stopped by mercuric chloride and the change determined polarimetrically. The velocity constants  $K$  and  $V$  were calculated by means of the formulae  $K = \frac{1}{t} \log \frac{C_0}{C_t}$  and

$$V = \frac{1}{t} \log \frac{C_0 + (C_0 - C_t)}{C_t},$$

in which  $C_0$  and  $C_t$  are the optical rotations at the beginning and after a time  $t$ . The values given by  $V$  were more constant. The quantity of dead yeast selected was such as to give about the same rate of fermentation of dextrose as the living yeast.

Doubling the quantity of either dead or living yeast doubles the rate of fermentation. Galactose was not fermented by the yeast chosen. The relative velocities of fermentation of dextrose, levulose, and mannose by the living yeast are 1:0.63:0.52, and by the acetone yeast, 1:1.06:0.81, indicating that the killing of yeast alters its relative fermentative activity towards the three sugars. The change may be attributed to an alteration in the permeability of the cell membrane or to the presence of different zymases within the cell. Adopting Harden and Young's view, the treatment with acetone either damages a substance which is important for the rapid fermentation of dextrose, but relatively less important for that of levulose.

E. F. A.

**Phosphorus Assimilation of Aspergillus Niger.** ARTHUR W. DAX (*J. Biol. Chem.*, 1911, 10, 77-80).—Raulin's medium was used with the ammonium phosphate omitted, and an equivalent amount of phosphorus in another form added. Excellent growth was obtained with anhydrous sodium orthophosphate, pyrophosphate, and metaphosphate. Sodium hypophosphite led to germination, but not growth, and sodium phosphite was not utilised at all. Excellent results were also obtained with various organic phosphorus compounds, namely, phytin, sodium glycerol phosphate, and nucleinate, lecithin, casein and avertinellin.

W. D. H.

**Behaviour of Certain Mould Fungi towards Organic Acids.** I. REGINALD O. HERZOG and O. RIPKE (*Zeitsch. physiol. Chem.*, 1911, 73, 287—289).—*Mycoderma cerevisiae*, *Monilia candida*, and *Oidium lactis* were grown for six weeks in solutions containing from 0.5 to 3% of a number of organic acids. They caused from 30% to 95% of the acid to disappear, being very selective in their behaviour. Mycelium killed with acetone and ether when kept under water through which a stream of air was passed developed more carbon dioxide in presence of acids, the acid being used up in the process. Mycelium treated with liquid air behaved quite similarly to the dead mycelium, although it had remained alive.

E. F. A.

**Behaviour of Certain Mould Fungi towards Organic Acids.** II. REGINALD O. HERZOG, O. RIPKE, and O. SALADIN (*Zeitsch. physiol. Chem.*, 1911, 73, 290—301. Compare preceding abstract).—*Mycoderma cerevisiae*, killed by acetone, when kept in solutions of acetic or lactic acid causes a disappearance of the acid, which is not oxidised, however, since the production of carbon dioxide is less in acid than in pure aqueous solution. Mandelic acid behaves similarly; the acid used up is not bound by the fungus, either by salt formation or by absorption, or converted into an ester, but it is chemically changed. There is no difference in behaviour between the two optical isomerides in the case of mandelic and tartaric acids. Living fungi give similar results with acids.

E. F. A.

**Behaviour of Certain Mould Fungi towards Amino-acids.** REGINALD O. HERZOG and O. SALADIN (*Zeitsch. physiol. Chem.*, 1911, 73, 302—307. Compare preceding abstracts).—The addition of leucine to a mycelium of *Penicillium glaucum*, previously kept in water until the respiratory daily output of carbon dioxide was steady, caused a definite increase in the daily production of carbon dioxide. This increase amounted to considerably more than was to be accounted for by the leucine which had disappeared. An exactly parallel behaviour was shown by a mycelium previously killed with acetone. Other amino-acids behave similarly in causing an increased production of carbon dioxide.

E. F. A.

**A Ferment Causing Bitterness in Wines, Acting as a Dehydrating Agent towards Glycerol.** E. VOISENET (*Compt. rend.*, 1911, 153, 363—365. Compare Abstr., 1910, ii, 738, 909).—A pure culture of the bacillus causing bitterness in wine has been obtained in a Laurent peptone medium. This has previously been shown to produce acraldehyde during fermentation. It appears to effect a direct, irreversible transformation of glycerol into acraldehyde without the formation of intermediate compounds. The organism is incapable of producing acraldehyde from butyric, lactic, or succinic acids, glyceraldehyde or dihydroxyacetone. The acids formed during fermentation have an inhibitory effect on the production of acraldehyde, but this proceeds further on the addition of calcium carbonate.

W. O. W.

The Erepsins of *Glomerella Biformis* and *Sphaeropsis Malorum*. HOWARD S. REAP and H. S. STAHL (*J. Biol. Chem.*, 1911, 10, 109—112).—Erepsins have previously been found by others in saprophytic fungi, but not in parasitic fungi. The two fungi named are parasitic and insect allies. The presence of erepsin was shown in both. The extracts of the mycelia also liquefy gelatin.

W. D. H.

Chemistry of Tuberculin. GEORG LOCKEMANN (*Zeitsch. physiol. Chem.*, 1911, 73, 389—397).—Various purified forms of tuberculin do not give the protein reaction. The bacilli were grown in a medium containing only one organic substance, namely, asparagine. The culture fluids were found to contain protein. The same is true for glycerol-bouillon media; but the preparation known as *endoxin* did not give a single protein reaction, and therefore does not contain the protein substances which pass during growth into the culture fluid.

W. D. H.

Action of Nitrogen on Wines. PHILIPPE MALVEZIN (*Bull. Assoc. chim. Sucr. Dist.*, 1911, 29, 73—75).—When nitrogen is passed through wine contained in a test-tube for a second, and the wine inoculated with *Mycoderma vini*, a turbidity is produced after about thirty-six hours. No turbidity is produced in wine merely inoculated.

Red wine which has been decolorised with animal charcoal, inoculated with *Mycoderma*, treated with nitrogen, and then heated for five minutes at 70—80°, acquires a blue colour when a few drops of tincture of guaiacum are added. When treatment with nitrogen is omitted, either no blue coloration is produced, or else a paler blue than in the nitrogen-treated wine.

If an excessive amount of nitrogen is employed, the oxidising action is checked, and the *Mycoderma vini* fails to develop.

When fermenting wines rich in sugar are saturated with nitrogen, left for a day or two, and filtered, fermentation is completely checked. The amounts of nitrogen employed were 20 grams per hectolitre.

N. H. J. M.

The Assimilation of Atmospheric Nitrogen by Thermophilic Bacteria. HANS PRINGSHEIM (*Centr. Bakt. Par.*, 1911, ii, 31, 23—27).—Cultures of these organisms were obtained by inoculating Winogradsky's solution with a little garden soil, and incubating under anaerobic conditions at 61°. Active fermentation set in after six days, and microscopical examination showed the presence of long bacilli and some plectridium forma. Sub-cultures could not be obtained until media containing soil extracts were used. In such media and with impure cultures, considerable quantities of nitrogen were assimilated, where 5 and 2.5 grams of dextrose per litre of nutrient solution were supplied, the respective amounts of nitrogen assimilated for each gram of sugar fermented were 3.0 and 6.2 mg.

H. B. H.

The Formation of Oxides of Nitrogen during Denitrification. SHIGERHIRO SUZUKI (*Centr. Bakt. Par.*, 1911, ii, 31, 27—49).—An

account of experiments carried out to throw light on some discordant results obtained by Beyerinck and Minkman (Abstr., 1909, ii, 1043), and to ascertain whether a production of nitrous oxide occurred when nutrient solutions other than nitrate bouillon were used.

It was found that accurate results could be obtained when the mixture of gases produced by fermentation was collected over mercury instead of calcium chloride solution, the oxygen absorbed by means of pyrogallol instead of by phosphorus, and the remaining gas burnt with pure oxygen and carbon monoxide in a Drehschmidt's platinum capillary tube. The percentage of nitrous oxide in the gas produced during denitrification was found to vary at different periods of the same fermentation, and to be dependent to a large extent on the composition of the nutrient solution. In all cases nitrous oxide, but not nitric oxide, was formed. High percentages of nitrate and high temperatures were favourable to the production of the former gas. H. B. H.

**The Formation of Nitric Oxide by *B. Hartlebii* during Denitrification.** A. J. LEBEDEF (Ber. Deutsch. bot. Ges., 1911, 29, 327—329).—Nitric oxide is evolved during the growth of *B. Hartlebii* under anaerobic conditions, and with the following culture solution: 1% of potassium sodium tartrate or sodium lactate, 0.3% of potassium nitrate, 0.05% of potassium dihydrogen phosphate, 0.02% of magnesium sulphate, and a trace of ferric chloride rendered slightly alkaline with potassium hydroxide. After three or four days at 26°, it is found that a considerable quantity of carbon dioxide is evolved, and a volume about one-twentieth as great of nitric oxide. On leading air into the flasks, brown fumes are seen. E. J. R.

**Plant Chemistry.** P. Q. KEEGAN (Chem. News, 1911, 104, 109—110).—From the results of analyses of about fifty wild plants, the conclusion is drawn that sugar is a highly important product of assimilation, that it is independent of starch, and is not a respiratory material and not convertible into acids. Sugar migrates in the plant, whilst starch does not.

An alcoholic extract of dried leaves of *Alliaria officinalis*, previously extracted with benzene, was found to contain a tannoid or a glucoside of a flavone derivative, which differs from all others by its reaction with iodine, indicating some form of hydroxybenzoic acid. It has no catechol or quinol nucleus, but probably a phloroglucinol complex.

Plants of the order *Compositæ* were found to contain a tannoid which contains a catechol nucleus, and, perhaps, a quinol nucleus. Other plants of the same order contain coffee tannin. The sub-order *Corymbiferae* seems to have most tannoid, and the *Cynarocephalæ* most tannin.

In connexion with the statement of Pichard (Abstr., 1899, ii, 788) that the presence of chlorides in the soil and the absorption by plants is antagonistic to the absorption of nitrates, it was found that seven micorhyza plants which contain no nitrates contained 9.8—28% of chlorine in the crude ash, whilst the same number of nitrate plants contained only 1.2—4%. On the other hand, some micorhyza plants were found to contain very small, and some nitrate plants considerable, amounts of chlorine. N. H. J. M.

**Formation of Nitrous Acid in the Vegetable and Animal Cell.** FURMAN MANN (*Compt. rend.*, 1911, 163, 357—360. Compare this vol., ii, 643).—The fresh juice from pea-stalks was precipitated with alcohol and filtered through a Chamberland filter. The sterile liquid thus freed from the organisms which produce nitrous acid described in a previous paper, still developed traces of this substance when allowed to remain, but was free from nitric acid. Etiolated plants furnished more nitrous acid than green ones, in one case 0.0093 gram per litre was obtained after twenty-four hours.

Washed blood-corpuscles when submitted to hæmolysis yield a liquid giving a distinct reaction with potassium iodide. Hence Jones' discovery of nitrous acid in normal urine was confirmed, but urine from a patient in an advanced stage of tuberculosis gave a negative result.  
W. O. W.

**The Relationship between Tanning Substance and Another Colloid in Ripening Fruits, Especially Phoenix, Achras, and Diospyros.** FRANCIS E. LLOYD (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 65—73).—It has been found that certain tannin cells, especially those of the pericarp of certain fruits, contain a second colloidal substance in addition to tannin. This appears to absorb the tannin during the process of ripening, and as a result of this absorption the tannin cannot be removed from the cells by extraction processes. The active colloid appears to be a carbohydrate which resembles the pectoses, and on hydrolysis yields a sugar.

In the unripe fruit the colloid is present in a mucous condition, which changes, however, during the ripening until a stiff gelatin-like mass is obtained. The structure of the tannin-colloid aggregate, is much more nearly like that of the colloid than that of tannin. It is supposed that this aggregate is of the nature of a solid solution, and that its formation is of primary importance in connexion with the ripening of fruits.  
H. M. D.

**Origin of Osmotic Effects.** IV. **The Differential Septa in Plants with Reference to the Translocation of Nutritive Materials.** HENRY E. ARMSTRONG and E. FRANKLAND ARMSTRONG (*Proc. Roy. Soc.*, 1911, B, 84, 226—229. Compare this vol., ii, 642).—In water, laurel or *Acacia* leaves remain unchanged for many days. When a substance, such as toluene, which can penetrate the leaf is added to the water, not only does the leaf change, but reducing sugar and other substances diffuse out of it. In a solution of hydrogen cyanide, however, although similar changes take place inside the leaf, no reducing sugar passes out into the solution.

Most leaves become brown and some black when exposed to water containing a little toluene; in a cyanide solution such coloration is very much less marked. These differences are interpreted as proof that differential septa which breakdown under the influence of most hormones remain intact when hydrogen cyanide is used, and it is suggested that the septa remain intact because the oxydase effect is eliminated in presence of hydrogen cyanide.

Oxidation processes are at a maximum in plants during the period

when light is inactive, and growth takes place chiefly during this period; the translocation of nutritive materials may take place because the septa are broken down and rendered permeable by oxidation; they may be repaired subsequently when assimilatory processes become ascendant. E. F. A.

The Action of Anaesthetics on the Osmotic Properties of the Plasma Membrane. W. W. LEFESCHKIN (*Ber. Deut. bot. Ges.*, 1911, 29, 349—355).—Treatment of a plant cell with an aqueous solution of an anaesthetic lowers the permeability of the plasma membrane; thus the isotonic coefficients of potassium nitrate for *Tradescantia discolor* were: after immersion in water, 2.95; in 0.1% chloroform water, 3.04, the corresponding permeability factors being 0.127 and 0.160 respectively. Immersion in 2.5% ether solution caused a still further lowering of permeability. In other words anaesthetics lead to an increase in osmotic pressure of the cell sap.

The bearing of these results on Nathanson's hypothesis of the Mosaic structure of the plasma membrane is indicated. E. J. R.

Absorption of Arsenic by Beetroots. HANS REMMLER (*Chem. Zeit.*, 1911, 35, 977—979).—The author has carried out a number of experiments in order to ascertain whether the spraying of beetroots with arsenical preparations for the destruction of parasites (*Silpha atrata*) leads to the absorption of appreciable quantities of arsenic by the beetroots. After removal of soil from beetroots which had been sprayed with a solution of Schweinfurt-green, the roots were found to contain 0.08 mg. of  $As_2O_3$  per kilogram. Other specimens contained less, the quantity appearing to depend on the amount of arsenical solution which reached the soil during the spraying. The beetroot leaves contained 0.25 mg. of  $As_2O_3$  per kilogram.

W. P. S.

The Action of Methylene-blue on the Respiration and Alcoholic Fermentation of Living and Killed Plants. WLADIMIR I. PALLADIN, ELISE HUBBENET, and MARIE KORSAKOFF (*Biochem. Zeitsch.*, 1911, 35, 1—18).—In the presence of air, etiolated stem tips of *Vicia faba*, which have been coloured with methylene-blue, excrete considerably more carbon dioxide than do uncoloured control tips. The tips from *Pisum sativum* are similarly effected by the dye, but to a less degree. Quinine has a similar action. On the seeds, however, the action in the two plants differs, in that methylene-blue stimulates slightly the respiration of the seeds of *Pisum sativum*, whereas quinine slightly diminishes it. The difference of action is explained by the difference in the amounts of respiratory chromogen, those materials containing small quantities of these substances being only slightly stimulated by methylene-blue, and being readily poisoned by quinine. The stimulating action of methylene-blue on *Vicia faba* ceases if the plant is killed by subjecting it to a low temperature. Other differences between the action of the methylene-blue on aerobic and anaerobic respiration are demonstrated. The ratio carbon dioxide/alcohol is about 1 in coloured plants, but less than 1 in the control plants.

Disodium hydrogen phosphate paralyzes the injurious action of methylene-blue on the etiolated-stem tips of *Vicia faba*. S. B. S.

**Direct Assimilation of Inorganic and Organic Forms of Nitrogen by Higher Plants.** HENRY B. HUTCHINSON and NORMAN H. J. MILLER (*Centr. Bakt. Par.*, 1911, ii, 30, 613-547. Compare Abstr., 1909, ii, 923).—Water-culture experiments, under sterilised conditions, with the apparatus previously described (*loc. cit.*), in which peas were supplied with nitrogen in various forms.

Of the substances employed, urea showed the greatest assimilation, one plant taking up 18.2 mg. of nitrogen. Barbituric acid (with calcium carbonate) was readily assimilated, being possibly converted in the plant into urea and malonic acid. Acetamide and alloxan were also readily assimilated, the former producing more growth than ammonium sulphate without calcium carbonate, whilst formamide, glycine, alanine, guanidine hydrochloride, cyanuric acid, and oxamide, although assimilated, were taken up in smaller amounts. The results obtained with trimethylamine, *p*-urazine [1:2:4:5-tetrazine], and hexamethylenetetramine were doubtful, as although one of the two plants showed a slight gain of nitrogen (especially with *p*-urazine and hexamethylenetetramine), there was no gain in dry produce. Hydroxylamine hydrochloride, ethyl nitrate, propionitrile, and methyl carbamate gave negative results, whilst tetranitromethane is toxic.

Soluble humus was readily assimilated, producing considerable growth. Peptone was also assimilated, but the dry produce was a good deal less than with humus.

N. H. J. M.

**Constituents of Apples.** CARL THOMAS (*J. pr. Chem.*, 1911, [ii], 84, 247-248).—By the distillation of apple-skins in steam and extraction of the resulting aqueous liquid, a soft mass is obtained, which yields a crystalline substance when moistened with alcohol; the alcoholic filtrate contains a yellow oil, having a refreshing odour of apples.

When treated with dilute sodium carbonate and extracted with ether, the skins yield a colourless, odourless, powdery substance, m. p. above 200°. This substance is not readily wetted by water, and in conjunction with a little plant-fat or gum, forms the covering which prevents the fruit from drying.

F. B.

**Chemistry of Polyporus frondosus.** MAX BAMBERGER and A. LANDRIED (*Monatsh.*, 1911, 32, 641-642).—The alcoholic extract of the fungus contains a basic nitrogenous substance which forms a colourless, granular powder. It dissolves readily in mineral acids, with which it gives crystalline salts. The hydrochloride and hydrobromide crystallise in transparent, rectangular columns and quadrate plates. The sulphate is specially characteristic, crystallising in glass-like needles. The nitrate, picrate, and platinichloride have been prepared. The salts do not become brown until heated above 300°.

E. F. A.

**Loss of Hydrocyanic Acid from Cherry-laurel Water on Keeping and on Treatment with Animal Black.** A. ASTRUC (*J. Pharm. Chim.*, 1911, [vii], 4, 5—13).—This paper is mainly of pharmaceutical interest. The results obtained show that to avoid loss of hydrogen cyanide from the cherry-laurel water of the French codex, the water should be stored in the dark in well-stoppered bottles holding from 125 to 150 c.c., and that the supply should be renewed frequently and its content of hydrocyanic acid determined from time to time.

Cherry-laurel water, which has become coloured, due to the action of air and light, should not be decolorised by animal charcoal, as this occasions large losses of hydrogen cyanide. The amount of acid absorbed by the charcoal varies with the quality of the latter, the strength of the water in acid, and the quantity of charcoal used, but is scarcely affected by the time the charcoal is left in contact with the water or the temperature (up to 80°) at which the operation is conducted.

T. A. H.

**The Sugar in the Nodules of *Nephrolepis hirsutula*, Presl.** G. DIETHELM LIEBER (*Ber. Deut. bot. Ges.*, 1911, 29, 375—380).—The nodules contained 4.3% of dry matter, of which 1.6 was sugar. Beyond the fact that the sugar is a hexose or mixture of hexoses, nothing more could be determined.

E. J. R.

**Chemical Examination of *Oenanthe Crocata*.** FRANK TUTIN (*Pharm. J.*, 1911, [iv], 33, 296—298).—The investigation was undertaken to ascertain the nature of the substance to which the well known toxic action of this plant is due. Poehl (*Arch. exp. Path. Pharm.*, 1895, 34, 258) has attributed this property to "enanthisotoxin," a neutral, amorphous product soluble in ether, and the author confirms this observation, but points out that the toxic material is ill-defined and amorphous, so that no formula can be assigned to it. In addition a number of physiologically inactive substances were isolated.

A concentrated alcoholic extract of the whole plant deposited sucrose on keeping. On steam-distillation the extract yielded (1) a volatile oil, b. p. 100—200°/100 mm.,  $D_{20}^{25}$  0.9381,  $n_D^{20}$  +1.516' in a 25 mm. tube, which was yellow, had an unpleasant odour, and gave the furfuraldehyde reaction; (2) a dark-coloured aqueous liquid, and (3) a brown resin. From the aqueous liquid salicylic acid, a crystalline substance, m. p. 83°, amorphous products, and a mixture of dextrose and levulose, probably resulting from inversion of sucrose, were obtained. The brown resin was resolved into its constituents by extraction successively with light petroleum, ether, chloroform, ethyl acetate, and alcohol. The portion soluble in light petroleum contained triacontane, hentriacontane, ipuranol, a phytosterol, probably sitosterol,  $C_{27}H_{48}O$ , palmitic acid, and a mixture of unsaturated fatty acids, chiefly linoleic acid. The portion dissolved by ether was a brown, sticky solid, of which about half was soluble in alkalis, the residue being a dull green, viscid mass, which became reddish-brown when heated with potassium hydroxide in alcohol.

The portions of the crude resin finally dissolved in turn by chloro-



form, ethyl acetate, and alcohol were black, amorphous solids, devoid of physiological activity when given to guinea-pigs in doses of 1 gram. This was also the case with the aqueous liquid, but similar doses of the light petroleum and ether extracts of the resin rendered guinea-pigs hyper-æsthetic, and marked convulsions with trismus soon appeared. Of the two portions of the ether extract, the neutral part was more active than the acidic portion, and the former probably corresponds with Poehl's "œnanthotoxin." No alkaloid or enzyme could be detected in any part of the plant.

T. A. H.

**Algerian Oleander Bark.** ALBERT LEULIER (*J. Pharm. Chim.*, 1911, [vii], 4, 157—161).—Dubigadoux and Durieu have shown already that the latex of this apocynaceous shrub contains a strophanthin-like glucoside, and the author confirms this and further characterises the glucoside.

The bark of the plant, which contains the latex, was used as a raw material, and Fraser's process was employed for the isolation of the glucoside (Abstr., 1887, 1115; 1888, 606; 1890, 262). It crystallises in minute, brilliant, pale yellow, irregular lamellæ, is intensely bitter, dissolves in water, alcohol or glycerol, is precipitated by tannin solutions, and becomes pasty at about 165°. It is hydrolysed by boiling with mineral acids, forming a reducing sugar and an amorphous bitter substance, m. p. 92° (approx.). A number of colour reactions of the parent glucoside are described. It is regarded as possibly a  $\psi$ -strophanthin (compare Feist, Abstr., 1900, i, 555).

T. A. H.

**Pot-culture Experiments.** JOHN A. VOELCKER (*J. Roy. Agric. Soc.*, 1910, 71, 343—350. Compare Abstr., 1908, ii, 622).—Small amounts of lithium salts (Li = 0.0018%) seem to have a stimulating effect on wheat; no injurious action was observed when the amount of lithium does not exceed 0.002%. Cesium salts may be employed in larger amounts (0.0036%) without injurious effects. Zinc salts are injurious to wheat when the soil contains 0.04% of zinc.

Experiments in which barley was grown in soil containing 0.02% of iron sulphate and varying amounts of manganese sulphate (0.005 to 0.06%) showed a slightly stimulating effect, but no clear differences due to the different amounts of manganese. Similar results were obtained when 0.02% of manganese sulphate and varying amounts of iron sulphate were applied to the soil.

N. H. J. M.

**Production of Nitrates in Arable Soils.** ALFRED KOCH (*J. Landw.*, 1911, 59, 293—315).—Drain-pot experiments on nitrification in different soils and subsoils, both alone and with addition of ammonium sulphate.

Comparing the amounts of nitrates produced in the surface soil, (20 cm.) and in the subsoil (20—40, 40—60, and 60—80 cm.), it was found that the amounts of nitrates decreased with the depth more than the percentages of total nitrogen. When ammonium sulphate was added to the soils, somewhat less nitrate was formed in the subsoils than in the surface soil during the first three months, whilst later on there was less difference.

Ammonium sulphate (2 grams per kilo. of soil) applied in November was nitrified to the extent of one-half by the following March, and completely nitrified by June.

As regards losses of nitrogen during the nitrification of ammonium salts, the results obtained with two different soils showed that 83—85% of the nitrogen applied was nitrified. In the case of subsoil (60—80 cm.) the amount of nitrogen recovered as nitrate amounted to only 78%. In addition to loss of nitrogen applied as ammonium salt, there was also a loss of soil nitrogen.

Application of lime to soils containing ammonium sulphate checks nitrification as long as an odour of ammonia is perceptible. Lime added to soil alone increased nitrification until converted into carbonate.

N. H. J. M.

**Behaviour of Manganese in the Soil Towards Some Agricultural Plants.** PAUL LEIDREITER (*Bied. Zentr.*, 1911, 40, 531—535; from *Inaug. Diss.*, Rostock).—The results of pot experiments in which oats were manured with various manganese compounds showed in every case an increased yield as compared with plants which received no manganese. The highest gain was obtained with manganese carbonate; pyrolusite and manganese phosphate gave the next highest results, whilst the least gain was obtained with the nitrate. Similar results were obtained with beans with small amounts of manganese, whilst larger amounts were injurious.

In experiments with mustard in sandy, loam, and humus soils, it was found that the effect of the different forms of manganese varies according to the nature of the soil. In sandy soil, pyrolusite and manganese carbonate gave the greatest gains. In loam the greatest and least gains were obtained with manganese hydroxide and pyrolusite respectively.

Further experiments with sugar-beet and mangolds grown in sandy loam showed increased yields of leaf and roots when manganese was applied. In the case of potatoes, manganese sulphate increased the yield both of tubers and starch.

Water-culture experiments with oats showed that manganese is injurious when 25 mg. per litre is present, and that the plants fail altogether in solutions containing 0.5 gram per litre.

Oats take up most manganese when applied in the form of nitrate, whilst beans take up more as phosphate than as nitrate.

N. H. J. M.

**Dihydroxystearic Acid in Good and Poor Soils.** OSWALD SCHREIBER and ELBERT C. LATHROP (*J. Amer. Chem. Soc.*, 1911, 33, 1412—1417).—The authors have isolated dihydroxystearic acid from soil by extraction with 2% sodium hydroxide solution. Examination of a number of soils shows it to be an almost invariable accompaniment of infertility; the soil conditions in which it is found are generally poor drainage, poor aeration, too great compactness, deficiency in lime, lack of good oxidation, and tendency for fungus development. It does not appear to be connected with any special crop.

The authors have already shown that the acid is harmful to plants in water cultures; they consider therefore that it is a direct factor in causing infertility, but it is not necessarily the only factor; it is, however, symptomatic of poor soil conditions.

E. J. R.

**The Availability of Nitrogenous Materials as Measured by Ammonification.** JACOB G. LIPMAN, PERCY E. BROWN, and IRVING L. OWEN (*Centr. Bakt. Par.*, 1911, ii, 31, 49—85).—The value of many organic fertilisers is determined, not so much by the actual amount of nitrogen as shown by chemical analysis, as by the rate at which the substance is broken down in the soil, that is, its availability. The present paper is an attempt to ascertain whether this availability can be gauged by ammonification, and how far the results so obtained agree with vegetation experiments.

Definite quantities of dried blood, tankage, and ground fish from different sources were mixed with 100 grams of loam and quartz sand, and, after being moistened, were incubated at 27° for several days. The ammonia was then estimated, and the results when calculated as percentages of the total nitrogen supplied showed, in many cases, close agreement with those obtained from pot experiments.

The ammonification of substances of vegetable origin depends largely on the carbon-nitrogen ratio. In the presence of substances rich in carbon there appears to be re-assimilation of the ammonia by bacteria and moulds.

Substances with a narrow carbon-nitrogen ratio are more rapidly and also more completely nitrified. This is shown in the following table:

*Proportion of Applied Nitrogen Recovered.*

Material applied.	Ammonification		Nitrification		Vegetation	
	Tests.	%.	Tests.	%.	Tests.	%.
Corn meal.....	2	12	—	—	8	31
Rice flour.....	1	72	—	—	6	17
Wheat flour.....	5	56	23	15	22	02
Rye flour.....	6	94	13	84	23	04
Cotton-seed meal.....	41	18	42	87	52	31
Linseed meal.....	46	06	49	07	44	18
Cow-pea meal.....	29	31	33	12	23	54
Soy bean meal.....	39	79	42	41	42	99

The presence of readily assimilable compounds does not seem to increase the ammonification of peat to any extent. The addition of sodium nitrate and ammonium sulphate gave slight gains, whilst with blood decreases of 7—18% of the total nitrogen occurred.

On the whole, the ammonification and vegetation tests show sufficient agreement to indicate that the former will be found useful in determining the availability of organic nitrogenous manures.

H. B. H.

## Analytical Chemistry.

**Apparatus for Electro-analytical Determinations with a Mercury Cathode.** PAUL BAUMANN (*Chem. Zeit.*, 1911, 35, 854—855).—Details are given of an improved form of the mercury cathode vessel described by Böttger (*Abstr.*, 1909, ii, 619), the object of the improvement being to facilitate the running-off of the electrolyte from the mercury at the end of the electrolysis, and also to trap any mercury or amalgam which may be carried over. This object is attained by inserting a stoppered tube, opening just above the level of the mercury, into the side and near the bottom of the vessel, there being a bulb in the tube between the stopcock and the vessel; the bulb acts as a trap for any mercury carried over.

The anode, which may be stationary or rotated, is a two-decker gauze electrode, similar in shape to the Hildebrand electrode (*Abstr.*, 1907, ii, 574), and strengthened by appropriate struts.

The apparatus may be used for separations by graded potential. It cannot be heated directly, for fear of breaking, so that when the heat generated by the current used for electrolysis is insufficient, a special heater must be used. This consists of a platinum wire heated electrically and enclosed in a glass tube filled with paraffin oil; the glass tube is then immersed in the electrolyte when heating is necessary.

T. S. P.

**Detection of Gas in Sealed-tube Reactions.** WILLIAM H. WARREN (*J. Amer. Chem. Soc.*, 1911, 33, 1417—1418).—The author seals on to the Carius tube a tap of the same glass, and is thus enabled to collect any gas formed during the reaction.

E. J. R.

**Estimation of Organic Matter in Waters by means of Permanganate.** HERMANN NOLL (*Zeitsch. angew. Chem.*, 1911, 24, 1509—1518).—The author's experiments show that in the estimation of organic matter in water by Kubel's method with permanganate, the direct action of sulphuric acid on permanganate and on any manganese dioxide formed is of no account so far as loss of oxygen is concerned. The sulphuric acid present hinders the formation of manganese dioxide from manganese sulphate and permanganate.

The interaction between manganese sulphate and permanganate takes place according to the equation given by Roscoe and Schorlemmer, namely,  $3\text{MnSO}_4 + 2\text{KMnO}_4 + 2\text{H}_2\text{O} = 5\text{MnO}_2 + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4$ . Manganese dioxide acts auto-catalytically on this reaction, but in water analysis, by Kubel's method, the catalytic effect is negligible.

In the determination of organic matter, the permanganate must always be in considerable excess, otherwise any manganese dioxide which may be formed will take part in the oxidation and the results will be too low. The addition of manganese sulphate to waters containing much chloride is therefore not to be recommended, since, the

formation of manganese dioxide is thereby increased. It is better in such cases to use Schulze's method.

The author considers that Kubel's method is satisfactory.

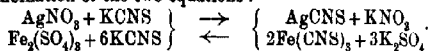
T. S. P.

**A New Reaction for the Detection of Hydrogen Peroxide.** O. VON SOBBE (*Chem. Zeit.*, 1911, 35, 898).—An ammoniacal silver nitrate solution is recommended for the detection of small quantities of hydrogen peroxide. A characteristic grey opalescence or precipitate is obtained. The test is even more delicate than the reaction with potassium iodide and starch usually employed.

L. DE K.

**Volhard's Method for the Estimation of Chlorine in Potable Waters.** A. T. STUART (*J. Amer. Chem. Soc.*, 1911, 33, 1344—1349).—In the determination of chlorine in drinking waters by Volhard's method, the author met with various discrepancies, which led to the following investigation. Two c.c. of silver nitrate solution (1 c.c. = 0.001 gram Cl) were added to 100 c.c. of water, and the solution titrated with potassium thiocyanate of strength equivalent to the original silver nitrate solution. Varying volumes (from 0.1 to 100 c.c.) of a 1% solution of ferric sulphate solution were added as indicator. It was found that various quantities of thiocyanate solution were required, the figures showing that in titrating 2 c.c. of silver nitrate, using 1 c.c. of indicators varying in strength from 1 to 10%, the readings may vary between 1.80 and 2.09 c.c. This represents an error not permissible for work of extreme accuracy, involving in its limits 2.9 parts per million of chlorine.

The error is caused by equilibria set up, which may be represented by a combination of the two equations:



The end point is also influenced by the dissociation of the ferric thiocyanate.

The conclusion is drawn that the method is only applicable in water analysis when very small amounts of silver nitrate, not greater than 0.2 c.c., in excess of that required are added.

Similar, but less, variations occur with *N*/10-solutions when large volumes of indicator solution are added.

T. S. P.

**Estimation of Iodine in Thyroid.** ATHERTON SEIDELL (*J. Biol. Chem.*, 1911, 10, 95—108).—A large number of estimations of iodine in the thyroids of different animals are given; a good deal of irregularity is noted, but the theory that this is due to seasonal influences is regarded as inconclusive. Although the Hunter method of analysis is admitted to be the best, the conclusions drawn from results obtained by the Baumann process are not invalidated.

W. D. H.

**Estimation of Small Quantities of Iodine in Animal Fluids.** R. BERNIER and G. PÉRON (*J. Pharm. Chim.*, 1911, [vii], 4, 151—157).—The application of the method already described for the

estimation of iodides (this vol., ii, 435) to organic liquids is rendered difficult in many cases by the presence of nitrites, formed by the action of permanganate on carbamide and other similar substances originally present in such products. The nitrites may be eliminated by the use of carbamide or ammonium salts in presence of acids. The following modification of the original process is given: Ten to twenty c.c. of urine, to which 0.5 gram of potassium hydroxide has been added, is evaporated to dryness in a nickel basin at 100°, and the residue calcined over a spirit lamp. The cold calcined residue is dissolved as far as possible in a little distilled water, the exhaustion of the soluble matter being completed with a 10% solution of sodium chloride. To the filtered extract potassium permanganate is added in excess, and the excess destroyed by alcohol. The cold solution is then made up to 110 c.c. and 100 c.c. of filtrate collected. To this 1 gram of ammonium chloride and 10 c.c. of acetic acid are added, and the whole boiled during five to ten minutes. The rest of the process is carried out as described previously (*loc. cit.*). The experimental difficulties met with in certain cases are described, with methods of overcoming them. The process is applicable to normal and pathological urines, blood, blood serum, and various liquids of the organism whether physiological or pathological in origin. A number of typical results with such fluids are quoted.

T. A. H.

**Estimation of Halogens in Organic Compounds.** THRONOR SR. WARUNIS (*Chem. Zeit.*, 1911, 35, 906—907).—The process may be applied in the case of solid substances or even liquids if they are not readily volatile. 0.2—0.3 Gram of the powdered substance is mixed in a spacious nickel crucible by means of a platinum wire with an intimate mixture of 10 grams of powdered potassium hydroxide and 5 grams of sodium peroxide. After putting on the lid, the crucible is heated in an air-bath at 75°, or at most 85°. When the mass begins to agglomerate, a gradually increased heat is applied by means of a very small flame until the mass has turned liquid, and it is kept in that condition for some time.

The fusion is dissolved in water, and gradually acidified with dilute nitric acid; if any iodine should be liberated, the solution should be decolorised by cautiously adding sulphurous acid. The halogen is then determined by means of silver nitrate, gravimetrically or volumetrically as usual.

L. DE K.

**Estimation of Halogens in Lipoids.** H. CAPFENBERG (*Pharm. Zeit.*, 1911, 56, 677).—One gram of the substance is placed in a porcelain crucible, a piece of cotton-wool is placed over it, and 10 c.c. of a 10% solution of potassium hydroxide in methyl alcohol are added. The contents of the crucible are evaporated to dryness at a temperature below the boiling point of the alcohol, then ignited over a low Bunsen flame for one hour, and the carbonised residue is dissolved in 100 c.c. of hot water. The solution is filtered, rendered acid with nitric acid, and the halogen is precipitated by the addition of silver nitrate.

W. P. S.

**Estimation of Dissolved Oxygen Absorbed by Sewage Effluents containing Nitrites and of Nitrites in Sewage Effluents and Water.** ROBERT W. CLARKE (*Analyst*, 1911, 36, 393—396).—*Estimation of Dissolved Oxygen Absorbed.*—The effluent is diluted, say, ten times with pure tap water, and five bottles of known capacity (300 c.c.) are completely filled therewith. The amount of oxygen present at the start and after one, two, and five days respectively is then determined by Winkler's manganese method (introduction of manganous chloride and sodium hydroxide containing potassium iodide; after acidifying with hydrochloric acid, the iodine liberated, which represents free oxygen, is estimated as usual). The author, however, recommends neutralising the free acid before titration with magnesium carbonate; nitrites will then not interfere. The difference in amount of free oxygen at the commencement and after a given interval gives the amount of oxygen absorbed.

*Estimation of Nitrites.*—A tall bottle holding 500 c.c. is filled with the nitrite-containing water or effluent to within 20 c.c. of the whole content. To this are added 4 c.c. of 33% manganese chloride, and 12 c.c. of the usual sodium hydroxide and potassium iodide solution with an extra gram of the latter are added. After shaking the stoppered bottle and allowing it to stand overnight, all free oxygen will have disappeared from the liquid, which, however, retains the nitrite. The clear liquid is now siphoned off into a 300 c.c. bottle, 3 c.c. of hydrochloric acid are added, and, after neutralising the excess of this with magnesium carbonate, the iodine liberated, representing the nitrite, is titrated with very dilute standard thiosulphate.

L. DE K.

**New Method of Estimating the Various Elements of an Organic Substance.** (1) Substance Containing  $C, H, O, N$ . (2) Substance Containing  $C, H, O, N, S$ . (3) Substance Containing  $C, H, O, N, S, Cl, Br, I$ . J. A. A. AUZIES (*Bull. Soc. chim.*, 1911, [iv], 9, 814, 815, 815—819).—For a substance containing carbon, hydrogen, oxygen, and nitrogen, the combustion tube, otherwise arranged in the ordinary manner, is filled with specially prepared thoria in place of cupric oxide. The water and carbon dioxide are collected in the usual way, and the nitrogen peroxide formed in the combustion is collected in a solution of cuprous chloride in hydrochloric acid, placed between the usual calcium chloride tube and the potash bulbs. The nitric peroxide formed is estimated by titrating the absorbent solution with standard stannous chloride.

When the substance to be burnt contains sulphur, a portion of the tube is filled with lead peroxide, or, better, the thoria and the lead peroxide are each enclosed in boats of special form. The sulphur is oxidised to sulphur dioxide by the thoria, and this is absorbed by the peroxide to form lead sulphate, which is determined gravimetrically.

When halogens are present, a third boat containing silver chromate is introduced. After the combustion is complete, the partly transformed chromate is treated with ammonia solution, which dissolves the chromate and chloride, the latter being recovered quantitatively by adding acetic acid to the solution and treating the precipitate with

potassium cyanide solution. The residue, insoluble in ammonia solution, is treated with potassium cyanide solution, which dissolves the silver iodide, but leaves the bromide unaffected. Results of simultaneous determinations of the eight elements by this process are quoted. The special boat recommended is figured in the original.

T. A. H.

The Hyperbolæ of Furnace Gas Constituents. ERNST LÁSZLÓ (*Chem. Zeit.*, 1911, 35, 994—996).—The author develops equations by means of which, having determined the percentage of carbon dioxide in furnace gases, the percentage of oxygen and nitrogen in the same can also be calculated, and also the ratio of the air passed into the furnace to that which is theoretically necessary for complete combustion. It is assumed that the ratio of nitrogen to oxygen in the air is known, and also the value of  $l$ , when the hydrocarbon burned has the formula  $C_mH_{lm}$ .

T. S. P.

Estimation of Silicon in Iron containing much Graphite. C. REICHARD (*Pharm. Zentr.-h.*, 1911, 52, 939—940).—One gram of the finely-divided iron is heated in a platinum crucible for fifteen minutes over a blast-flame, or for one hour over a Bunsen flame, and then dissolved in 25% hydrochloric acid. The solution is decanted from the small quantity of insoluble matter, and the latter is treated with fuming nitric acid. After the two acid solutions have been mixed together, the insoluble graphite is collected on a filter, washed, and ignited in an atmosphere of oxygen. The portion of the silica which remains in the acid filtrate is estimated in the usual way.

W. P. S.

The Oxidation of Hydrazine. V. Reaction between Potassium Iodate and Hydrazine Sulphate. C. F. HALE and H. W. RUSFIELD (*J. Amer. Chem. Soc.*, 1911, 33, 1353—1362. Compare Brown and Shetterly, *Abstr.*, 1910, ii, 233, 568).—The authors show that the oxidation of hydrazine sulphate by potassium iodate proceeds quantitatively in accordance with the equation given by Rimini (*Abstr.*, 1906, ii, 897), namely,  $5N_2H_4.H_2SO_4 + 4KIO_3 = 5N_2 + 12H_2O + 2K_2SO_4 + 3H_2SO_4 + 2I_2$ . In each experiment carried out the excess of iodate was determined, and also the volume of nitrogen evolved. The reaction is the same, whether the hydrazine is added to the potassium iodate in the cold (in an atmosphere of carbon dioxide) or at the boiling temperature (in an atmosphere of steam).

The method of procedure recommended is as follows: About 0.3 gram of the hydrazine salt is dissolved in 50 c.c. of water in a 300 c.c. narrow-mouthed conical flask. A measured volume of potassium iodate solution (7.1045 grams per litre) is then added, so that there are 5—10 c.c. in excess. The solution is diluted to 200 c.c., and boiled for thirty minutes over a free flame to expel the iodine. After cooling, potassium iodide and dilute (1:4) sulphuric acid are added, and the liberated iodine is titrated with  $N/10$ -thiosulphate.



The chief disadvantage of the method lies in the length of time required for the expulsion of the liberated iodine. T. S. P.

**Estimation of Nitric Nitrogen in Gun Cotton, Nitroglycerol, and Similar Products.** HENRI PELLET (*Ann. Chim. anal.*, 1911, 16, 294—296).—Schloessing's apparatus is preferred. In the case of gun-cotton or saltpetre (used for a check experiment) the substance is placed in the flask containing distilled water, which is then boiled until all the air has been expelled. A solution of ferrous ammonium sulphate strongly acidified with hydrochloric acid is introduced from the funnel tube, and the nitric oxide expelled on boiling is collected and measured.

In the case of substances which suffer volatilisation on boiling, such as nitroglycerol or nitric ethers, the iron solution is placed in the flask, and, after expelling the air by boiling, the nitrate is gradually added in dilute solution from the funnel tube. L. DE K.

**Estimation of Nitrites in Waters.** GUSTAVE BLANC (*J. Pharm. Chim.*, 1911, [vii], 4, 205—212).—It is shown that Trommsdorff's method is bad in principle, since the nitric oxide formed by the interaction of zinc iodide with nitrous acid is oxidised in contact with the air, forming more nitrous acid, which reacts with more of the iodide, so that the amount of iodine liberated and titrated may be far in excess of that corresponding with the amount of nitrite originally present. Test analyses confirmed this. Griess' method, on the contrary, was found experimentally not to be subject to any error of this kind. T. A. H.

**Some Sources of Error in the Gasometric Estimation of Nitrates and Nitrites by Schloessing's or Piccini's Methods.** OTTO RUFF and EWALD GERSTEN (*Zeitsch. anorg. Chem.*, 1911, 71, 419—426).—The presence of arsenites or sulphides in a solution of nitrates or nitrites gives rise to errors in the gasometric estimation. In the estimation of nitrates, in which an acid solution of ferrous chloride is required, the presence of arsenites causes a loss of nitric oxide, owing to the formation of nitrous acid, which passes over into the nitrometer. Arsenites only reduce nitrates in acid solution. Nitrites may be estimated satisfactorily, even in presence of arsenites, if the solution is kept neutral. Sulphides, however, prevent the estimation of nitrates or nitrites, the nitrous acid being partly reduced to ammonia. C. H. D.

**The Quantity of Nitric Acid Present in Wines.** J. TILLMANS (*Zeitsch. Nahr. Genussm.*, 1911, 22, 201—207).—The author finds that nitric acid is a natural constituent of practically all German wines, the quantity present varying from a mere trace to 18.75 mg. ( $\text{N}_2\text{O}_5$ ) per litre. The detection of nitric acid in wine does not, therefore, indicate the presence of added water in the wine. The diphenylamine-sulphuric acid method was employed for the estimation of the nitric acid; this method has been described previously (this vol., ii, 767).

but in the case of wine it is necessary to evaporate the diluted sample after the addition of animal charcoal in order to remove substances which interfere with the reaction, the estimation being then made on the evaporated solution diluted with water to its original volume.

W. P. S.

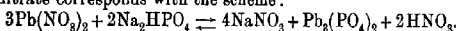
**Estimation of Phosphorus in Wine.** JEAN DORMANE (*Bull. Assoc. chim. Sucr. Dist.*, 1911, 29, 63—67).—The total phosphorus in wine is estimated by treating the dry residue from 200 c.c. with calcium hydroxide and heating on a sand-bath. It is then powdered, placed in a platinum boat, and heated in a porcelain tube in a current of air. The portion of the porcelain tube behind the platinum boat is filled with potassium carbonate. The whole tube is heated for two to three hours. The ash and the alkali are dissolved in dilute hydrochloric acid, and the phosphates estimated by means of ammonium-magnesium solution.

In estimating the phosphorus as phosphates, the residue from 100 c.c. of wine is extracted with cold dilute hydrochloric acid, and the phosphates in the filtrate precipitated in the usual manner.

The same process is employed for estimating the organic phosphates, except that the residue is boiled for an hour and a-half with stronger hydrochloric acid. The amount of phosphorus present as inorganic phosphates is deducted from the results.

N. H. J. M.

**Titration of Phosphoric Acid.** M. WAGENAAR (*Pharm. Weekblad*, 1911, 48, 845—850).—For determining the three hydrogen ions of phosphoric acid, the author recommends the following procedure: For the first ion the solution is tinted red with methyl-orange, and titrated with alkali until yellow; for the second, the titration is repeated after addition of phenolphthalein to the yellow reaction-mixture; for the third, excess of lead nitrate is added, and the rose-red solution titrated with sodium hydroxide. The action of the lead nitrate corresponds with the scheme:



A. J. W.

**The Alkalimetry of Magnesium Ammonium Phosphate and Acidimetry of Ammonium Phosphomolybdate.** FRANZ HUNDES-  
HAGEN (*Zeitsch. öffentl. Chem.*, 1911, 17, 283—294, 302—309, 322—324).—The author again recommends his titration process (*Abstr.*, 1895, ii, 84), which, however, had been previously worked out by Stolbe, and consists in washing the ammonium magnesium phosphate obtained in the usual way with alcohol until free from ammonia; the precipitate is then dissolved in a slight excess of standard acid, and the solution titrated with standard sodium carbonate, using methyl-orange as indicator. Twenty-five test analyses are given, showing the accuracy of the method. If arsenic acid is suspected, a previous separation of this substance should be effected by means of hydrogen sulphide, or else its amount present in the precipitate must be determined and allowed for. One c.c. of *N*/10-acid = 0.003552 gram of phosphoric anhydride, or 0.002016 gram of magnesium oxide. When

the process is applied in the so-called "citrate method," the triple phosphate should be purified by re-dissolving it in hydrochloric acid, and reprecipitating it with ammonia, after adding a little of the usual citrate solution and a little magnesium mixture; it will then be free from calcium and fit for titration.

Good results are also obtained by the author's well-known molybdate method, in which the yellow precipitate is dissolved in standard alkali, the excess of which is then titrated with standard acid, using phenolphthalein or litmus as indicator. One c.c. of *N*-alkali = 0.003078 gram of phosphoric anhydride. Operators are again reminded of the precautions to be taken to ensure the formation of a pure yellow precipitate. A microscopical test will prove the presence or absence of free molybdic acid.

L. DE K.

**Estimation of Arsenic in Toxicological Analysis.** W. NEY (*Pharm. Zeit.*, 1911, 615—616).—A weighed quantity of the substance, such as a portion of an animal organ, is distilled with 100 c.c. of hydrochloric acid, D 1.19, 2 grams of potassium bromide, and 5 grams of hydrazine sulphate until the mixture has been reduced to a syrupy consistence. The distillate is received in 200 c.c. of water, and the arsenic trichloride is then titrated with iodine solution in the presence of sodium hydrogen carbonate.

W. P. S.

**Treatment of Insoluble Residues.** ERICH EBLER (*Zeitsch. anal. Chem.*, 1911, 50, 610—614).—Lead chloride, together with any lead sulphate, is best removed by heating the insoluble matter with ammonium nitrate (40 c.c. of ammonia, D 0.925, and 67 c.c. of nitric acid, D 1.3325). Complex cyanides and insoluble (ignited) oxides may, generally, be rendered soluble by fusion at not too high a temperature with potassium hydrogen sulphate; the mass is then extracted with water containing a few drops of hydrochloric acid. The filtrate is tested as usual for metals, and the undissolved matter is examined for silver by treating with dilute sulphuric acid and a little zinc. When reduction is complete, the precipitate is washed with hot water and the excess of zinc and the silver are dissolved in dilute nitric acid; the silver is then tested for as usual.

The residue, which may contain antimonious oxide, stannous oxide, stannic phosphate, and perhaps silica, is collected, ignited, and weighed. It is then fused in a covered crucible at a gentle heat with two or three times its weight of the usual sulphur-potassium carbonate mixture. The mass is extracted with hot water, and the solution is treated according to one of the usual methods for the separation of tin, antimony, etc.

It is advisable to examine the undissolved portion of the fusion for alkaline earths and silica. This is done by fusing with anhydrous sodium carbonate over the blow-pipe. The mass is extracted with water, and both solution and residue are then examined by the usual methods for silica and alkaline earths respectively.

L. DE K.

**Separation Scheme without the Use of Hydrogen Sulphide.** ERICH EBLER (*Zeitsch. anal. Chem.*, 1911, 50, 603—609).—A slight modification of the process described some time ago (Abstr.,

1906, ii, 126). It is recommended first to remove the arsenic by distilling the mixture with fuming hydrochloric acid with addition of hydrazine bromide; the arsenic is then tested for in the distillate. In the presence of complex cyanides these are destroyed by boiling for half an hour in a reflux condenser with a mixture of equal volumes of fuming nitric and hydrochloric acids. Before applying the course without the use of hydrogen sulphide, the hydrochloric acid\* is expelled by repeated evaporation with nitric acid.

Uranium remains with the alkaline earths as a complex hydroxylamine compound of uranic acid, but is readily separated by a process communicated previously (Abstr., 1908, ii, 987); the alkaline earths are separated by the author's hydrochloric acid process (Abstr., 1909, ii, 347), but instead of a hardened filter an asbestos filter is now recommended.

The alkalis should be tested for in a separate portion of the mixture. The method used for silicates (heating with ammonium chloride and calcium carbonate) will be found very suitable. L. DE K.

**Method for the Reduction of Potassium Platinichloride in the Estimation of Potassium by the Platinum Process.** A. FRECHTER (*Zeitsch. anal. Chem.*, 1911, 50, 629—632).—The author recommends the process based on the reduction of the potassium platinichloride by means of magnesium ribbon and dilute hydrochloric acid at the boiling point, using only a few drops of acid at first. If 1 gram of the substance guaranteed to contain 5% of  $K_2O$  is taken for analysis, 0.2 gram of magnesium ribbon is required; for 20%, 0.5, and for 50%  $K_2O$ , 0.8—1 gram of magnesium will be sufficient. L. DE K.

**Estimation of Calcium Nitrate and Calcium Nitrite.** ALBERT STUTZER and Goy (*Chem. Zeit.*, 1911, 35, 891).—In the estimation of calcium nitrite and nitrate in the technical products made by the combustion of atmospheric nitrogen, Busch's method (Abstr., 1906, ii, 392) gives unsatisfactory results, and the authors prefer to estimate the nitrite by titration with permanganate and then to estimate the total nitrogen in the oxidised liquid with "nitron."

Since "nitron" is very expensive, the authors recommend that the total nitrogen be determined by reduction to ammonia with Devarda metal (50% Cu, 45% Al, 5% Sn) and distillation of the ammonia into excess of standard sulphuric acid. T. S. P.

**Analysis of "Nitrolime."** HUBERT KAPPEN (*Chem. Zeit.*, 1911, 35, 950—952).—A series of experiments from which it appears that the total nitrogen in "nitrolime" is best estimated by treating 0.5 gram of the sample with 10 c.c. of water before boiling with 30 c.c. of sulphuric acid (Kjeldahl process). Addition of sodium thiosulphate, salicylic acid, and zinc dust does not seem to produce the effect expected by Monnier. Full particulars are found in the tables of the original paper.

For the estimation of cyanamide nitrogen, Perotti's silver process is recommended. In recently prepared samples the results agree very

well with the total nitrogen according to Kjeldahl. Old and badly stored samples often contain dicyanodiamide. In the absence of dicyanodiamidine it is best estimated by Caro's process (this vol., i, 119).  
L. DE K.

**Extraction of Gases from Copper by a Chemical Method and the Estimation of Oxygen.** MARCEL GUICHARD (*Compt. rend.*, 1911, 153, 272—275).—Commercial copper is shown to contain sufficient dissolved oxygen to vitiate estimations of this gas carried out by its means. Fine copper wire previously heated at 600° in a vacuum for a long time should be used for the purpose. A specimen of copper liberated about twice its volume of gas when heated with iodine in a vacuum.  
W. O. W.

**Detection of Mercury in Urine. II.** ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1911, 73, 401—406. Compare this vol., ii, 771).—The "end" solution is prepared in the manner previously described (this vol., ii, 771), and the mercury removed from it by leaving in the warmed solution for an hour or more two or three strips of copper foil about 0.1 mm. thick. These become grey when much mercury is present; they are removed, washed, and dried, care being taken to handle them only with forceps. They are next placed in a clean dry test-tube, which is moderately heated and allowed to cool; the foil is shaken out, a trace of iodine introduced, and the tube warmed until the iodine vapours fill two-thirds of it. The formation of the red mercuric iodide takes place slowly, but is very characteristic.

E. F. A.

**The Use of Sulphur Monochloride in the Determination and Analysis of the Rare Earth Minerals.** WILLIAM BROOKS HICKS (*J. Amer. Chem. Soc.*, 1911, 33, 1492—1496).—Fergusonite was completely decomposed by the action of the vapours of sulphur monochloride, not a trace of metallic acids remaining in the residue, and no rare earths being detected in the volatile portion. Eschynite and euxenite were also readily decomposed, whilst a picked sample of samarskite was decomposed to the extent of 98.78%.

In carrying out the decomposition, the minerals were placed in a porcelain boat in a combustion tube, which was heated while the vapours of sulphur monochloride were passed through it. The volatile chlorides of the metallic acids passed into the receiver, whilst the non-volatile chlorides or oxychlorides of the earth metals remained in the boat.

The principal advantages of this method of decomposition are the ease with which it takes place, the cheapness of the apparatus, and the separation of columbium, tantalum, titanium, and tungsten from the rare earths during the decomposition. The chief disadvantage is that the excess of sulphur monochloride is mixed with the volatile chlorides, but it may easily be overcome by allowing the mixture to pass into dilute nitric acid, and then removing the precipitated sulphur by adding excess of ammonium hydroxide and hydrogen sulphide.

- In the non-volatile portions of the above minerals, search was made for scandium, but none was found. Fergussonite contained, however, 2–3% of thorium, whilst yttrium and thorium were found in eschynite.

T. S. P.

**A New Method for the Separation of Cerium.** CHARLES JAMES and L. A. PRATT (*J. Amer. Chem. Soc.*, 1911, 33, 1326–1330).—The authors have found that potassium bromate is capable of oxidising cerous nitrate in faintly acid or neutral solution, so that this element may be entirely separated from the other rare earths. The solution of the rare earth nitrates is boiled with potassium bromate in the presence of a lump of marble, the cerium being entirely precipitated as the basic ceric nitrate, with varying amounts of basic ceric bromate. When the operation is carefully conducted, the cerium thus obtained is free from the other rare earths. In working on a large scale with concentrated solutions, it is advisable to use a slight excess of the bromate, and to stop the action while about 1% of the cerium remains in the liquid. Under these conditions, a cerium product is obtained, which, after washing with a 5% ammonium nitrate solution, gives a pale straw-coloured oxide. A saturated solution of the nitrate of this material shows no trace of absorption spectrum when tested with a layer 20 cm. thick.

The above method may be employed for the gravimetric estimation of cerium. The cerium salt is precipitated twice, in each case until the mother liquor gives no test for cerium with hydrogen peroxide; the precipitate is washed with a 5% solution of ammonium nitrate. After the second precipitation the precipitate is dissolved in hydrochloric acid, the cerium precipitated as oxalate, and weighed as oxide.

Details are given of the application of the method to the purification of cerium on a large scale from the monazite earths which have been freed from thorium.

T. S. P.

**Analysis of Monazite Sands.** GABRIEL CHESNEAU (*Compt. rend.*, 1911, 153, 429–431).—The best methods hitherto published having proved unsatisfactory, the following process, which avoids difficulties caused by the sparing solubility of thorium phosphate in acid, was devised and found to give good results.

2.5 Grams of the sand are fused with 15 grams of fusion mixture until all glistening particles disappear. The mass is extracted with boiling 1% sodium hydroxide (solution A). The residue is treated with hot 5% hydrochloric acid (solution B), and the process repeated on the insoluble portion. The final residue ( $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{SiO}_2$ ) and solution A ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ ) are analysed in the usual way. Solution B, freed from lead and copper, is diluted until it contains exactly 4% of hydrogen chloride, then treated with 4 grams of crystallised oxalic acid for every 100 c.c., and allowed to remain for two days. The filtrate is examined in the usual way for  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , Fe, etc., and the oxalates of the rare earths calcined below  $500^\circ$ ; the oxides are dissolved in nitric acid, with addition of hydrogen peroxide if necessary. After evaporating to dryness and dissolving the residue in 150 c.c. of water, thorium is separated by double precipitation with hydrogen peroxide,

according to Wyruboff's method. The reagent should be free from phosphates, and is advantageously treated with a little ammonium nitrate to avoid formation of colloids. The filtrate is made up to 500 c.c., and the rare earths precipitated in 100 c.c. Cerium is estimated in another 100 c.c. by Job's method, for which details are given.

A monazite sand from Madagascar gave on analysis:  $\text{ThO}_2$ , 5.5;  $\text{CeO}_2$ , 22.6;  $\text{La}_2\text{O}_3$ ,  $\text{Di}_2\text{O}_3$ , 25.0;  $\text{Y}_2\text{O}_3$ , etc., 0.8;  $\text{ZrO}_2$ , 1.6;  $\text{Fe}_2\text{O}_3$ , 3.7;  $\text{Al}_2\text{O}_3$ , 0.8; Mn, trace;  $\text{MgO}$ , 0.4;  $\text{CaO}$ , 0.5;  $\text{P}_2\text{O}_5$ , 23.5;  $\text{SiO}_2$ , 8.8;  $\text{TiO}_2$ , 6.7; loss on ignition, 0.4. Total 100.3. W. O. W.

**Precipitation of Aluminium, Chromium, and Iron by Ammonium Nitrite.** ERIK SCHIRM (*Chem. Zeit.*, 1911, 35, 979—980).—Although sodium nitrite may be used in place of ammonium nitrite in the process described previously by the author (*Abstr.*, 1909, ii, 834), it has the disadvantage that alkalis cannot be estimated subsequently in the same portion of the sample. Manganese may be separated from iron by means of sodium nitrite, provided that a small quantity of ammonium sulphate be added to prevent precipitation of the manganese. A double precipitation is, however, recommended in this case. The manganese is then precipitated from the filtrate by means of ammonium persulphate. W. P. S.

**Estimation of Manganese as Manganous Oxide, Manganomanganic Oxide, and Manganese Sesquioxide.** PAUL N. RAIKOW and P. TISCHKOFF (*Chem. Zeit.*, 1911, 35, 1013—1015).—Manganese may be converted quantitatively into manganous oxide by heating the higher oxides in a rapid current of hydrogen, using a Rose's crucible. The higher oxides may be converted quantitatively into manganomanganic oxide by ignition in a slow current of carbon dioxide. Manganese may also be converted quantitatively into manganese sesquioxide by ignition of the oxides or the carbonate in a current of oxygen.

Manganous sulphate may be converted into the sesquioxide by heating alternately in a current of hydrogen and in air, and finally igniting in a current of oxygen. L. DE K.

**Ferric Sulphate as a Standard for Titrating Potassium Permanganate.** JAROSLAV MILBAUER and OTTO QUADRAT (*Zeitsch. anal. Chem.*, 1911, 50, 601—603).—One gram of pure ferric sulphate is dissolved in an Erlenmeyer flask in 25 c.c. of water and 10 c.c. of sulphuric acid, and, after adding a few granules of iron-free zinc, the whole is heated gently until everything has dissolved. An equal volume of water is added, and the solution titrated with permanganate.

Ferric sulphate is best prepared by boiling 10 grams of ferrous sulphate for about an hour with 100 c.c. of sulphuric acid. When cold, the bulk of the acid is poured off through a Gooch crucible, and the remainder removed by washing with alcohol, and then with anhydrous ether. Finally, the salt is dried in a water-oven to constant weight.

L. DE K.

**Volumetric Estimation of Ferric Salts with Permanganate after Reduction with Zinc.** ERICH MÖLLER and GUSTAV WEGELIN (*Zeitsch. anal. Chem.*, 1911, 50, 615—623).—When using pure zinc, or zinc in contact with platinum, for the reduction of ferric salts, it is necessary to wait until the zinc has completely dissolved, otherwise there will be a small quantity of iron deposited on the undissolved zinc. This inconvenience may be avoided by working as follows: 100 c.c. of the ferric iron solution (or a smaller volume diluted to 100 c.c.) are mixed with 5 c.c. of sulphuric acid and five to ten drops of *N*-copper sulphate. After adding three or four amalgamated zinc rods (5 cm. in length and 0.6 cm. in diameter), the solution is heated for about two hours at 100° in a current of carbon dioxide. The copper solution need only be added in the first experiment.

L. DE K.

**Precipitation of Iron with Hydrazine Hydrate.** ERIK SCHIRM (*Chem. Zeit.*, 1911, 35, 897).—The iron solution containing about 0.1 gram of iron is diluted to 250—300 c.c. If necessary, a few drops of hydrochloric acid and a little bromine are added, and the excess of the latter is boiled off. A large excess of ammonia is added, and then a few drops of hydrazine hydrate, which causes the precipitate to turn into a fine, granular black powder, which subsides rapidly and is free from sulphate. After washing and drying, it is ignited, finally over the blast, to constant weight. The filtrate may be used for estimating the sulphate.

Experiments to estimate iron in the presence of zinc by means of hydrazine hydrate are, as yet, unsuccessful.

L. DE K.

**Simplified Apparatus for Estimating Carbon in Iron.** G. BUTZBACH and G. FENNER (*Chem. Zeit.*, 1911, 35, 917).—Two apparatus of the usual type are described and figured. In the first one the condenser is fixed to the flask containing the oxidising liquid by means of a rubber cork, which cannot be affected by spiriting acid, and is rendered more effective by a water seal.

In the second one the flask is connected with the condensing tube, by means of a ground joint. In both there is an absence of the usual side-tubes, thus rendering them less liable to breakage.

L. DE K.

**Employment of Combustion under Pressure in the Estimation of Carbon in Steels.** P. MAHLER and E. GOUTAL (*Compt. rend.*, 1911, 153, 549—551).—The sample of steel contained in a refractory crucible free from calcium carbonate is burnt in oxygen in a calorimetric bomb similar to those employed in determining the calorific power of coal, but having a capacity of about 1 litre. The carbon dioxide is absorbed by barium hydroxide, and estimated by titration. Results given by this method agree closely with those obtained by the copper chloride and combustion process. W. O. W.

**Rapid Estimation of Total Carbon [in Iron and Steel].** H. DE NOLLY (*Rev. de Métallurgie*, 1911, 8, 391—395).—The iron or



steel, in the form of fine drillings, is introduced into an asbestos capsule, supported in a litre flask of Jena glass, which is closed with a rubber stopper and supplied with oxygen under a pressure of 30 to 40 cm. of water. The flask contains a measured volume of a 0.4% solution of sodium hydroxide. The metal is ignited by passing a current of 10–15 amperes between a pair of electrodes. When combustion is complete, the flask is shaken to absorb carbon dioxide, and the solution is titrated with sulphuric acid (1 c.c. = 1 mg. of carbon) and phenolphthalein. White cast iron, ferro-silicon, and other brittle alloys are mixed with lead peroxide before ignition. Grey cast iron gives low results, owing to incomplete combustion of the graphite. C. H. D.

**Apparatus for the Estimation of Sulphur in Iron and Steel.** D. A. WENNMANN (*Chem. Zeit.*, 1911, 35, 863).—Diagrams are given of two apparatus made entirely of glass, so that all rubber connexions are avoided. T. S. P.

**Rapid Estimation of Ferric Oxide in Cement.** A. GOLDBINZEFF (*Chem. Zeit.*, 1911, 35, 961–962).—Two grams of the sample are placed in an Erlenmeyer flask, moistened with 10 c.c. of water, and allowed to remain for ten minutes, when another 75 c.c. of water and then, while shaking, 100 c.c. of *N*-hydrochloric acid are slowly added. The shaking is continued until the greater part of the cement has dissolved, when the solution of the remainder is effected by heating the liquid to boiling; the boiling is then continued for three to five minutes to expel any hydrogen sulphide. The solution is reduced by sulphur dioxide, the excess of which is then boiled off in a current of carbon dioxide. After some fifteen minutes, the exit tube is closed with a piece of rubber and clamp without interrupting the current of carbon dioxide, and the flask is cooled in cold water. The iron is titrated, as usual, with *N*/10-permanganate after adding 8–10 c.c. of a solution of manganese sulphate. L. DE K.

**Estimation of Ferrocyanides and Thiocyanates.** LÉON RONNET (*Ann. Chim. anal.*, 1911, 16, 336–337).—The solution is strongly acidified with hydrochloric acid, and a slight excess of a hot solution of ferric chloride is added. After heating for half an hour on the water-bath, the Prussian-blue is collected and washed with hot water. The filter and contents are then transferred to a graduated flask and treated with a sufficiency of 10% solution of potassium hydroxide, and, after being kept for twelve hours with frequent shaking, the whole is made up to a definite volume with water, and a known volume of the filtrate is then acidified with dilute sulphuric acid and titrated for ferrocyanide with *N*/10-permanganate as usual. One c.c. permanganate = 0.0422 gram of crystallised potassium ferrocyanide.

The filtrate from the Prussian-blue is made up to a definite volume, and an aliquot portion is heated on the water-bath with addition of a slight excess of sodium hydrogen sulphite. Solution of copper sulphate is then added in slight excess, and after half an hour the cuprous thiocyanate is collected and washed. The filter and contents

are then placed in a flask, and the precipitate is dissolved in dilute ammonia (1:2). The solution is acidified with dilute sulphuric acid, and, while still warm, titrated with  $N/10$ -permanganate; 1 c.c. = 0.001616 gram of potassium thiocyanate.

L. DE K.

**Quantitative Separation with "Cupferron."** OSKAR BAUDISCH (*Chem. Zeit.*, 1911, 35, 913).—"Cupferron," so useful in the separation of iron from copper, not being readily procurable, the author recommends analysts to prepare it themselves. It is not explosive.

Sixty grams of nitrobenzene, 1000 c.c. of water, and 30 grams of ammonium chloride are well stirred, and to the white emulsion is added 80 grams of zinc dust in very small quantities, so that the temperature keeps between  $16^{\circ}$  and  $18^{\circ}$ . When the odour of nitrobenzene has completely disappeared, the solution is drawn off from the zinc hydroxide, and, after cooling to  $0^{\circ}$  by means of ice, the liquid is saturated with salt, which causes an abundant crystalline precipitate of phenylhydroxylamine. It may be observed that great care must be taken not to let this substance come in contact with the skin, as it is very poisonous. After draining and removing the mother liquor by means of filter paper, the compound is dissolved in 300–500 c.c. of ordinary ether, and after cooling the filtrate to  $0^{\circ}$ , a current of gaseous ammonia is passed for ten minutes and an excess of amyl nitrite is added. An abundant separation of nitrosylphenylhydroxylamine ammonium ("cupferron") takes place, which is drained, washed with ether, and then pressed between filter paper. It is advisable to place in the stock bottle a lump of ammonium carbonate.

L. DE K.

**The Separation of Iron and Vanadium by the Ether Method.** EUGEN DEISS and HANS LEYSANT (*Chem. Zeit.*, 1911, 35, 869–871, 878–879).—Rothe's ether method (compare Blair, *Abstr.*, 1908, ii, 900) for the separation of iron from other elements cannot be used in its original form for the separation of iron and vanadium, since ether extracts appreciable quantities of vanadium from hydrochloric acid solutions, especially when the vanadium is in the quinquevalent condition. Solutions of quadrivalent vanadium do not give up any vanadium to ether so long as care is taken that reducing agents are present to prevent the oxidation of any vanadium by peroxide usually contained in ordinary ether. In ordinary practice it is not convenient to have such reducing agents present, since they would also reduce the ferric salts. Advantage is therefore taken of the fact that pervanadates are insoluble in ether. After the chief extraction has been carried out by Rothe's method, the ethereal extract, containing the ferric salt and some vanadium, is further shaken several times with ether-hydrochloric acid (hydrochloric acid,  $D=1.10$ , saturated with ether), to which a little hydrogen peroxide has been added. The hydrogen peroxide oxidises the vanadium to pervanadates, which then pass into the aqueous layer.

The many details necessary in carrying out the method are fully described.

T. S. P.

**Estimation of Iron, Ammonia, and Nitrous Acid in Waters** by means of the Autenrieth-Koenigsberger Colorimeter. KARL SÜPFLE (*Arch. Hygiene*, 1911, 74, 176—184).—The above colorimeter is strongly recommended in water analysis.

Iron is estimated by the thiocyanate-ether process, ammonia by Nessler's reagent after removing alkaline earths, and nitrites are estimated by *m*-phenylenediamine and sulphuric acid; if necessary, the alkali earths and colouring matters are removed by adding a mixture of sodium carbonate and hydroxide. L. DE K.

**Rapid Detection of Elements Furnishing Sulphides Insoluble in Dilute Acids.** M. EMMANUEL POZZI-ESCOR (*Bull. Soc. chim.*, 1911, [iv], 9, 812—814).—The mixed sulphides, precipitated by hydrogen sulphide from dilute acid solution, are treated with 25% hydrochloric acid, furnishing (1) a solution which may contain lead, antimony, tin, cadmium, and zinc, and (2) a residue, which may contain copper, molybdenum, arsenic, bismuth, mercury, gold, and platinum.

The solution is treated with ammonia, which precipitates the first three metals, and leaves cadmium and zinc in solution, where they can be detected by the usual tests. The precipitate, which may contain lead, antimony, and tin, is dissolved in hydrochloric acid, and these elements sought for by the usual tests.

The residue, insoluble in hydrochloric acid, is treated with nitric acid, which dissolves copper, molybdenum, arsenic, and bismuth, and leaves undissolved mercury, gold, and platinum, which are then obtained in solution with *aqua regia*. The elements are then sought for in these two solutions by the usual tests. The process is stated to give trustworthy qualitative results more rapidly than that in general use. T. A. H.

**Assay of Wolfram Concentrate.** H. W. HUTCHIN (*Analyst*, 1911, 86, 398—403).—A recapitulation of the four chief methods for the assay of commercial wolfram. In the *aqua regia* methods, the tungstic acid is finally obtained by ignition of ammonium tungstate or mercurous tungstate. In the soda digestion and fusion processes, the tungstic acid is finally obtained by ignition of mercurous tungstate.

All four methods seem to be very satisfactory; the old *aqua regia* ammonium tungstate method has, perhaps, most to commend it, as it allows of operating on 1 to 2 grams, whereas the other methods are limited to quantities of about 0.5 gram of the sample. L. DE K.

**The Action of Salicylic Acid on the Metallic Acids.** JOHN HUGHES MULLER (*J. Amer. Chem. Soc.*, 1911, 33, 1506—1510).—Solutions of sodium or potassium columbate, tantalate, thorate, and zirconate are precipitated quantitatively by salicylic acid, whereas titanium is not so precipitated; this difference is used as the basis of a method for the quantitative separation of titanium from the other elements.

Alkali titanates give an intense yellow colour on the addition of salicylic acid; the reaction is extremely delicate, and may be used for the colorimetric determination of this metal. The colour is destroyed by traces of hydrofluoric acid or of fluorides, and is affected by traces of iron. Zirconium gives a brownish tinge to the solution, which is also affected by large quantities of columbium. The effects of the rare earths, etc., are also described, and the colorimetric method is applied to the estimation of titanium in the presence of columbium, tantalum, or thorium.

Five % solutions of sodium tungstate or molybdate are not precipitated by salicylic acid, and the resulting solution gives no precipitate with ammonium hydroxide. Titanium is precipitated under such conditions, but the reaction cannot be used to separate titanium from tungsten and molybdenum.

T. S. P.

**The Detection of Small Quantities of Alcohol in Fermenting Liquids.** ALB. KLÖCKER (*Centr. Bakt. Par.*, 1911, ii, 31, 108—111).

—In the systematic study of yeasts, one of the most important characteristics is the capacity of the organism to ferment different sugars. Where vigorous fermentation occurs, the usual qualitative tests may be employed, but even in cases where no apparent fermentation takes place, the author considers it necessary that actual tests should be made, and describes a modification of Pasteur's drop method, by means of which traces of alcohol may be detected.

Five c.c. of the liquid to be tested are poured into a test-tube 180 mm. long and 24 mm. wide. This is closed with a cork bearing a glass tube 180 mm. long and 3 mm. wide, which is allowed to protrude slightly on the lower side of the cork. The whole is then placed vertically over a flame with wire gauze, and is heated gently, care being taken that bumping does not occur. If alcohol is present, characteristic oily drops appear in the tube; the lower the amount of alcohol, the higher being the point at which these drops occur.

It is claimed that by the use of this method, 0.002—0.001% of alcohol can be detected.

H. B. H.

**Estimation of both Phenol and *p*-Cresol in Urine.** MAX SIEGFRIED and R. ZIMMERMANN (*Biochem. Zeitsch.*, 1911, 34, 462—472. Compare this vol., ii, 72).—The urine, after being made alkaline with sodium hydroxide, is evaporated to 1/5th of its bulk, acidified with sulphuric acid, and then distilled in steam. To separate volatile acids from phenols, the distillate is made alkaline with sodium hydrogen carbonate, and distilled in steam in a current of carbon dioxide. The reducing substances are separated then by Neuberg's method by means of lead acetate and sodium hydroxide, and then, after distillation of these substances, the phenols are distilled off after acidification with sulphuric acid. The phenol and cresol are then estimated by the method already given by the authors, which they find preferable to that of Kossel and Penny. The analyses of mixed urines from several individuals showed that 1.5 litres contained 0.0260 gram of *p*-cresol and 0.0186 gram of phenol; 58.1% of the total phenols consisted

therefore of *p*-cresol. The details are given of the experiments on which the analytical method is founded. S. B. S.

**Estimation of Phenols in the Urine of Oxen.** PAUL LIECHTI and W. MOOSER (*Zeitsch. physiol. Chem.*, 1911, 73, 365—370. Compare Neuberg and Hildesheimer, *Abstr.*, 1910, ii, 1116).—Polemical. The supposed formation of furfuraldehyde on distillation of herbivorous urine with phosphoric acid, derived from dextrose, pentose, or paired glycuronic acid, is shown not to take place. The Kossler-Penny process advocated by Neuberg and Hildesheimer (*loc. cit.*) leads to far larger errors than any neglect of the furfuraldehyde formed. The substitution of phosphoric acid for sulphuric acid in the distillation prevents the formation of urogon, which otherwise fixes iodine; further aldehydes present are not hydrolysed in such a way as to affect the estimation of the phenols. E. F. A.

**Estimation of Volatile Acids in Wine.** KARL WINDISCH and THEODOR ROETGEN (*Zeitsch. Nahr. Genussm.*, 1911, 22, 155—170).—It is recommended that 50 c.c. of the wine should be distilled in a current of steam until 200 c.c. of distillate have been collected; if the distillation is continued beyond this, considerable quantities of lactic acid are found in the distillate. When the wine contains more than 0.2 gram of volatile acids per 100 c.c., it should be diluted with an equal volume of water, and 50 c.c. of the mixture taken for the estimation. The volume of the steam must be so regulated that the wine is first evaporated to 25 c.c. and maintained at this volume until the end of the distillation. The time taken for the distillation is about thirty minutes; the steam should be under as low a pressure as possible, and it is advisable to employ a still-head filled with glass beads in order to reduce the distillation of the lactic acid to a minimum. W. P. S.

**Employment of the Electrometric Method for the Estimation of the Acidity of Tan Liquors.** II. JOSEPH T. WOOD, HENRY J. S. SAND, and DOUGLAS J. LAW (*J. Soc. Chem. Ind.*, 1911, 30, 872—876).—A hydrogen electrode is described for use in the electrometric method of estimating the acidity of tan liquors (this vol., ii, 233); slight improvements in the general form of the apparatus are proposed, and experimental details and results are recorded. W. P. S.

**Analysis of Liquids containing a Large Quantity of Tartaric Acid and Small Amounts of Glycerol and Tannin.** G. HINARD (*Ann. Falsif.*, 1911, 4, 391—397).—Having experienced certain difficulties in the analysis of solutions containing about 100 grams of tartaric acid, 10 grams of glycerol, and 3 grams of glycerol per litre, the author gives the following methods for the estimation of these constituents and of the total solids of the solution. The total solids may be estimated by drying 5 c.c. of the solution on pumice-stone over sulphuric acid and under as low a pressure as possible; at the end of twenty-four hours, the temperature of the desiccator is raised to 50°, and the drying is continued over phosphoric

oxide to constant weight. For the estimation of the glycerol, 100 c.c. of the solution are treated with sufficient potassium hydroxide to convert the tartaric acid into potassium hydrogen tartrate; the latter is removed by filtration, and the filtrate is evaporated at a low temperature after the addition of freshly prepared lead hydroxide. The residue is extracted with hot alcohol, the solution filtered, excess of lead is precipitated as carbonate, and an equal volume of ether is added, together with a few grams of potassium carbonate. The solution is then filtered, evaporated, and the residue dried under reduced pressure. The tartaric acid may be estimated by the methods used in wine analysis, and the tannin is estimated iodometrically.

W. P. S.

**Estimation of Milk Fat by Count of the Fat Globules.** H. P. T. OERUM (*Biochem. Zeitsch.*, 1911, 35, 18—28).—The relationship between the number of fat globules in a given measure, the transparency of the milk (the experimental method for determining which is described), and the fat content is mathematically worked out. The conclusion is drawn that each observer must obtain his own formula for each kind of milk, and the method has, therefore, no immediate practical value.

S. B. S.

**Assay of Chloral.** L. BOURDET (*J. Pharm. Chim.*, 1911, [vii], 4, 18).—The author suggests that in assaying chloral by the method prescribed in the French Codex, (1) distilled water, freed from carbonic acid, should be used; (2) a control experiment with water and alkali alone should be made; (3)  $N/2$ -alkali should be substituted for  $N$ -alkali, and (4) the time of contact of the alkali with the chloral should be reduced to fifteen minutes.

T. A. H.

**Ulex's Process for the Estimation of Nicotine in Tobacco Extracts and Nicotine Salts.** JULES KESNER (*Ann. Chim. anal.*, 1911, 16, 339—341).—A recapitulation of Ulex's process (treatment of the extract with a mixture composed of aqueous sodium hydroxide, calcium oxide, and plaster of Paris, removal of ammonia fumes in a desiccator over sulphuric acid, distillation with water, and titration of the nicotine with standard acid), which the author strongly recommends for technical purposes. The author carries out the distillation and titration as follows: The mass is placed in a 3-litre distillation flask containing  $2\frac{1}{2}$  litres of boiled water, 10 grams of sodium hydroxide and 10 grams of paraffin (to prevent frothing) are added, and the whole is submitted to distillation. Six portions of 1000, 500, 200, 100, 100, and 100 c.c. respectively are collected and titrated separately with  $N/2$ -hydrochloric acid, using delicate litmus solution as indicator; 1 c.c. of acid = 0.081 gram of nicotine.

L. DE K.

**Comparative Studies on the Nicotine Estimations in Tobacco Extracts.** JULIUS TÓTH (*Chem. Zeit.*, 1911, 35, 926—927).—At the author's suggestion, J. KRAMPERA analysed a sample of tobacco extract by the methods of Kissling, Ulex, Degrazia, and Tóth,

and the results are given in a table; in a second table are given the results of analyses made by the methods of Kissling, Koenig, Tóth, and the modified process of the latter. This consists in substituting xylene for toluene in the extraction of the nicotine; the results obtained by titration and polarisation are very concordant.

On the whole, the author has reason to prefer his own modified process.

L. DE K.

**Estimation of Quinine as Acid Citrate in Certain Organic Liquids.** THOMAS COCKBURN and J. W. BLACK (*Analyst*, 1911, 36, 396—398).—A slight modification of Nishi's process for the estimation of quinine in urine (Abstr., 1909, ii, 710). Two hundred and fifty c.c. of urine are rendered alkaline with concentrated aqueous sodium hydroxide and extracted three times with ether. The ethereal extracts are washed with small quantities of water, evaporated, the residue dried and dissolved in 20 c.c. of anhydrous ether, and the solution is filtered into a weighed flask with which has also been weighed a small asbestos filter tube, and the undissolved matter is washed with small quantities of ether. The quinine is now precipitated by adding 10 c.c. of a saturated ethereal solution of citric acid, and the closed flask is left for twenty-four hours. The ether is then poured off through the filter-tube, and the deposit is washed thrice in succession with 10 c.c. of ether, D 0.720. The tube is then placed in the flask, and the whole is dried, first gently, finally at 100°, and re-weighed; 100 parts of the acid citrate = 62.79 parts of quinine.

The process may be used in the presence of caffeine, but not of other cinchona alkaloids.

L. DE K.

**Separation of Urobilin by means of Talc and its Detection.** C. CABREZ (*Ann. Chim. anal.*, 1911, 16, 337—339).—The urine is defecated by mixing 45 c.c. with 30 c.c. of Denigès' mercury reagent, and to 30 c.c. of the clear filtrate is added 1 gram of talc, which on shaking removes all the urobilin; the talc is then at once collected on a filter and washed with water. In order to prove the presence of the urobilin, the talc is treated on the filter with 5 or 10 c.c. of Oliveri's reagent (zinc chloride 10 grams, ammonia 30 grams, strong alcohol 80 grams, ethyl acetate 20 grams), when at once a filtrate is obtained presenting a beautiful green fluorescence and exhibiting in the spectro-scope very neatly the band  $\gamma$ .

Or the talc may be treated with 10 c.c. of alcohol containing 5% of hydrochloric acid. To the filtrate is then added 5—6 c.c. of chloroform and 100—150 c.c. of water, and the whole is well shaken. The chloroform layer separates readily, and is then removed and filtered through a small filter moistened with chloroform. On adding an alcoholic solution of zinc acetate (1:1000), a green fluorescence is gradually formed, and the band  $\gamma$  is more distinct than before.

L. DE K.

**Estimation of Amino-groups in Amino compounds and in Urine and a Method for the Analysis of Proteins.** DONALD D. VAN SLYKE (*Ber.*, 1911, 44, 1684—1692; *J. Biol. Chem.*, 1911, 10, 15—55. Compare this vol., ii, 164, 779, 780).—Glycine, cystine, and

guanosine give high values when treated by the method already described.

Carbamide reacts slowly with the nitrous acid solution, and this reaction must be allowed for in estimating the amino-acid nitrogen in urine. After removal of ammonia from the urine made alkaline with sodium hydroxide solution, two estimations are made of the amino-acid nitrogen, one after six minutes and the other after the mixture has been left for twelve minutes. The difference between the two gives the error due to the reaction of the carbamide, and can be subtracted from the result given by the six minute determination.

Full details are given of a somewhat revised scheme for the analysis of proteins by the method of hydrolysis and nitrogen determinations. The following substances have been treated in this way: gliadin, edestin, hair, gelatin, fibrin, hæmocyanin, hæmoglobin, and the results are expressed in percentages of ammonia nitrogen, melanin nitrogen, cystine-, arginine-, histidine-, lysine-nitrogen, amino-nitrogen of filtrate, and non-amino-nitrogen of filtrate. Gelatin and hæmoglobin did not give any cystine nitrogen.

J. J. S.

**An Inner Anhydride Reaction of Albumin.** BRUNO BARDECK (*Chem. Zeit.*, 1911, 35, 634).—The author's iodoform process (this vol., ii, 826) when applied to albumins shows that these give very intense anhydride reactions.

L. DE K.

**Rapid Gravimetric Estimation of Urinary Albumin.** E. SIMONOT (*Bull. Soc. chim.*, 1911, [iv], 9, 839—842).—This method, which depends on the coagulation of the albumin by metaphosphoric acid, is stated to afford complete precipitation of the albumin in a form in which it can be easily and rapidly filtered, and washed (compare Denigès, *Abstr.*, 1893, ii, 248).

Five grams of sodium metaphosphate are dissolved in cold water, and made up to 100 c.c., or 5.70% grams of the metaphosphate may be dissolved by boiling in water during five minutes and made up to 100 c.c. as suggested by Denigès (*Chim. Anal.*, 3rd Edit., 1907, p. 1011). A preliminary trial having shown that the urine contains more than 0.5 gram albumin per litre, enough to yield about 10 grams is taken, filtered, made up to 100 c.c. if necessary, heated on the water-bath during ten minutes (during fifteen minutes if the quantity is 200 c.c.), and then for every 100 c.c. of liquid, 5 c.c. of the metaphosphate solution and 1 c.c. of hydrochloric acid are added and the heating continued during five to ten minutes. The coagulum is filtered on a dry tared filter and washed with boiling water until free from hydrochloric acid, and then twice with alcohol and once with ether. As much liquid as possible is removed by gentle pressure, and the coagulum dried at 110—120°. The weight, re-calculated for 1 litre of urine and multiplied by 0.88, gives the amount of albumin per litre in the urine examined.

T. A. H.

**Estimation of Lecithin.** C. VIRCHOW (*Chem. Zeit.*, 1911, 35, 913—914).—The author has slightly modified his process. One gram of the substance is boiled three times in succession, with 10 c.c. of



absolute alcohol, and the filtrate and washings, measuring about 50 or 60 c.c., are distilled off. After removing the last traces of alcohol by blowing, the weighed residue is dissolved in 10 c.c. of absolute ether, which is then poured through an asbestos filter tube; the residue is then washed three times with ether.

The ether is distilled off, and the weighed residue treated with 3—4 c.c. of fuming nitric acid; the solution is transferred to a platinum dish, and the flask rinsed three times in succession with 2 c.c. of fuming nitric acid. After evaporating the acid on the water-bath, the residue is mixed with 1 gram of dry sodium carbonate, using a platinum spatula. Five grams of the usual potassium nitrate-sodium carbonate mixture are now added, and the whole is heated to fusion for four to five minutes. The fusion contains the phosphorus of the lecithin as phosphoric acid, which is then estimated by the usual magnesia process.

L. DE K.

**A Method for Ash Analysis.** KARL STOLTE (*Biochem. Zeitsch.*, 1911, 35, 104—107).—The essential feature of the method consists in ashing the dried organic substance in a platinum basin placed inside a larger porcelain basin but kept from direct contact with it by pieces of porous plate, or an inverted crucible lid.

S. B. S.

**A New Colour Reagent for Callose.** M. TAVERT (*Compt. rend.*, 1911, 153, 503—505).—The reagents hitherto in use for callose are slow in action; the following one is very rapid. A 1% aqueous solution of resorcinol, containing 0.1% of concentrated ammonia, is allowed to remain for several days exposed to the air. It gradually undergoes oxidation, and gives rise to a blue substance apparently identical with Würster's resorcinol-blue, which the author calls *resoblue*.

Resoblue does not stain cellulose, but in thirty to sixty seconds it imparts a deep blue colour to callose. It can also be mixed with other stains to give double reactions; thus the mixture with Congo-red is stable, and colours callose blue and cellulose red. Other mixtures are also suggested.

E. J. R.

**Use of Nickel Hydroxide in Tannin Estimation.** PURAN SINGH (*J. Soc. Chem. Ind.*, 1911, 30, 936—937).—Results of experiments carried out by the author indicate that nickel hydroxide may be employed as a substitute for hide-powder in the analysis of tanning materials. The figures obtained were in fair agreement with those found when hide-powder was used.

W. P. S.

**Application of the Bromo-derivative Methods for the Assay of Vulcanised Rubber Wares.** WARNER EICH (*Chem. Zeit.*, 1911, 35, 971—972).—The process in use is based on the following assumptions: (1) 136 parts of rubber hydrocarbons absorb 319.7 parts of bromine or 64 parts of sulphur; (2) if 136 parts of hydrocarbons have already absorbed 32 parts of sulphur (in consequence of vulcanisation), only 159.85 parts of bromine can be taken up; (3) the sulphur absorbed is not acted on by bromine solutions; (4) if from the

total weight is deducted the combined sulphur and the bromine absorbed, the value of the rubber substance present is obtained; (5) from 64 parts of combined sulphur or from 319.7 parts of bromine absorbed, the presence of 136 parts of rubber hydrocarbons may be deduced.

According to the author's experiments, these assumptions cannot be entertained, and the process is therefore quite untrustworthy.

L. DE K.

**Estimation of the Specific Gravity of very small Quantities of Milk.** ALLOIS KAZIDL and EMIL LENK (*Biochem. Zeitsch.*, 1911, 35, 166—168).—As fat is not extracted from milk by simple mixture with a lipid solvent, the specific gravity can be determined by dropping the milk into mixtures, such as benzene-chloroform, benzene-carbon tetrachloride, etc., and finding the specific gravity of the mixture in which the milk neither sinks nor floats.

S. B. S.

**A New Modification of the Forensic Chemical Test for Blood.** OTTO VON FÜRTH (*Zeitsch. angew. Chem.*, 1911, 24, 1625—1628).—In testing for blood, the author recommends a combination of Leer's pyridine test with the leucomalachite-green test (Adler, *Abstr.*, 1904, ii, 459). The object to be tested is boiled for some minutes with a few drops of 50% potassium hydroxide to which a few drops of alcohol have been added. After cooling, the liquid is extracted with pyridine. The pyridine layer is separated, and again shaken with concentrated potassium hydroxide, after which about 1 c.c. of the solution is run on to a filter paper laid on a glass plate. This is then tested with the leucomalachite-green solution, to which has previously been added 1% of hydrogen peroxide.

A full discussion of the sensitiveness of the test and of any errors which may occur is given.

T. S. P.

**Meyer's Reagent for the Detection of Blood.** A. SARTORY (*Compt. rend.*, 1911, 152, 131—133).—The red coloration produced by blood in presence of hydrogen peroxide with phenolphthalein previously reduced by zinc, is also given by alkali hydrogen carbonates. The test cannot therefore be taken as specific for blood, and should only be used as a confirmatory test.

W. J. Y.

**Estimation of Gelatin.** W. GREIFENHAGEN, J. KÖNIG, and A. SCHOLL (*Biochem. Zeitsch.*, 1911, 35, 217—227).—Beckmann's formaldehyde method is of little practical value. Precipitation by Nessler's reagent by Vamvaka's method brings down all the gelatin, but it also precipitates proteoses. Although trichloroacetic acid (Obermayer's method) only produces a turbidity with dilute solutions of gelatin, it does not completely precipitate proteoses, and this reagent therefore cannot be employed for separating these substances from gelatin. Mercuric chloride solution does not produce a quantitative separation, but if it precipitates the same amount of nitrogenous matter as zinc sulphate, the conclusion may be drawn that gelatin is not present.

Mercuric iodide can also be employed as a precipitant. If the solution is first precipitated by zinc sulphate, the precipitate redissolved, and mercuric iodide in acetone or alcohol added (with precautions described in detail by the authors) and a precipitate is then produced which contains a large proportion of the nitrogenous matter which was precipitated by the zinc sulphate, then it may be deduced that gelatin is present. A satisfactory method for separating gelatin from proteoses does not exist. S. B. S.

**Analyses of Liquorice Juices.** L. GADOIS and J. GADOIS (*Bull. Soc. chim.*, 1911, [iv], 9, 741—743).—The analyses of liquorice juices by different methods having furnished discrepant results, the following analytical method was adopted: The moisture was estimated by drying at 100°, insoluble matter by two extractions with cold water for twenty-four hours, and the ash by ignition. The glycyrrhizin was determined by precipitating the resinous matter from aqueous solution with alcohol, concentrating the filtrate, and precipitating with hydrochloric acid in a weighed beaker, the precipitate being washed with water, treated with ammonia, and the ammonium derivative dried at 100°. W. G.

**A New Method for the Detection of Salvarsan** (Diaminodihydroxyarsenobenzene). J. ABELIN (*Munch. Med. Woch.*, 1911, 19. A Reprint).—A very little of the salvarsan is dissolved in 2—3 c.c. of water, and the yellow solution is decolorised by addition of 3—4 drops of dilute hydrochloric acid. After cooling the solution, 3—4 drops of a 0.5% solution of sodium nitrite are added, when a diazo-compound is formed, showing a vivid yellowish-green fluorescence. The liquid is now added, drop by drop, to a 10% solution of resorcinol, to which an excess of sodium carbonate has been added, when a beautiful red colouring matter will be formed; care must be taken that the liquid remains alkaline.

When applying the process to urines, 7—8 c.c. of the sample are acidified with 5—8 drops of dilute hydrochloric acid, and when cold, 3—4 drops of the above sodium nitrite solution are added. A few drops of the liquid are then added to 5 c.c. of the alkaline resorcinol solution, or the ring test may be applied successfully.

Atoxy, treated as above, yields an orange colouring matter.

L. DE K.

**Pyro-Analyses of Drugs.** LEOPOLD ROSENTHALER (*Ber. Deut. pharm. Ges.*, 1911, 31, 333—346).—A microscopical and chemical investigation of crystalline sublimes obtained in vacuum from a number of drugs. Probably it would be better still to subject their extracts to the sublimation process. For the micro-illustrations and properties of the various sublimes, the original paper should be consulted.

The following drugs were examined: *Cortex chinæ*, *Folia uvae ursi*, *Cortex frangulæ*, *Cortex cascaræ sagradæ*, *Rhizoma rhei*, *Gallæ*, *Rhizoma hydrastis*, *Opium*, *Cubebæ*, *Semen calabari*, *Piper nigrum*, and *Præcis anisi*. L. DE K.









